

# THERMAL DECOMPOSITION OF *n*-PENTANE. II\*

## EFFECT OF UNSATURATED PRODUCTS AND MECHANISM OF THE REACTION

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(Received: July 10. 1971)

The pyrolysis of *n*-pentane has been investigated at 520°C at initial pressures of 200 torr in the presence of ethylene, propylene and butene-1, respectively. The composition of the products was strongly altered in the presence of olefines. The effect has been explained by addition reactions between alkyl radicals and olefines.

### Introduction

In the investigations of thermal decomposition of simple saturated hydrocarbons, significant self-inhibition was observed in some cases. The self-inhibition was generally explained by the reactions between chain carrier radicals and some unsaturated products. Inhibition by propylene and *i*-butene was observed in the pyrolysis of *n*-pentane [1, 2]. LEATHARD and PURNELL pointed out that only the addition of hydrogen atoms to olefines can bring about self-inhibition [3].

In order to study the inhibiting effects of unsaturated products in the pyrolysis of *n*-pentane, experiments were carried out in the presence of added unsaturated products, *i. e.* ethylene, propylene and butene-1.

### Experimental

The applied system and method have been described previously [4]. 200 torr of *n*-pentane and different quantities of ethylene, propylene or butene-1 were mixed and admitted into the reaction vessel at 520°C. Samples were taken at different stages of the reaction and analysed by a Carlo Erba Fr. Mod. C. gas chromatograph, equipped with a thermal conductivity detector. The products of the reaction were identified on a Finnigan 1015 mass spectrometer combined with a gas chromatograph. Propylene and ethylene were taken from cylinders, and distilled three times at low temperature. Butene-1 was prepared from butanol by catalytic dehydration. Butene-1 contained 5 per cent *cis*- and *trans*-butene-2 as impurities.

\*Part I: Acta Phys. et Chem. Szeged 17, 33 (1971).

### Results and Discussion

**Effect of Ethylene.** The following effects of added ethylene have been observed.  
1. Added ethylene increased the initial rate measured manometrically and by gas chromatography (Fig. 1).

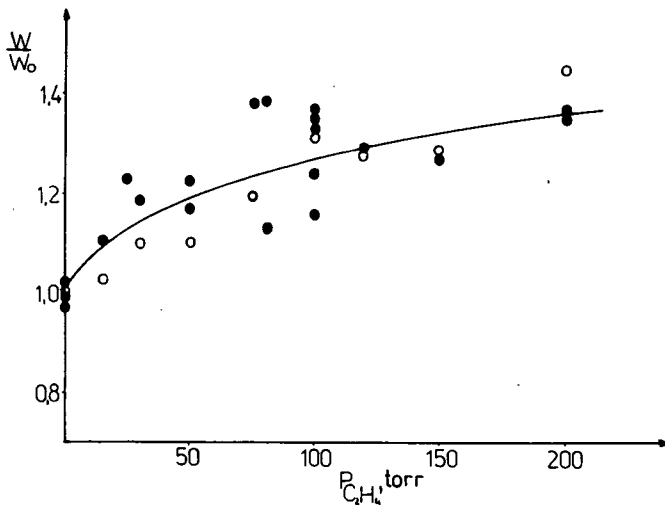


Fig. 1. Effect of ethylene on the initial rate measured manometrically (●) and by gas chromatography (○). Initial pressure of pentane 200 torr,  $T = 520^{\circ}\text{C}$ .

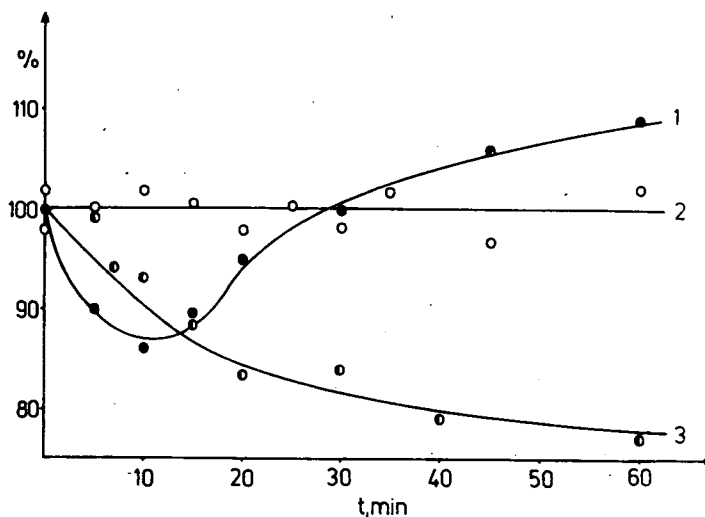


Fig. 2. The measured quantities of ethylene (1), propylene (2), and butene-1 (3), as a function of time in the influenced reactions, expressed as the percentage of the initially added quantities of olefines. Initial pressures: ethylene 50 torr, propylene 200 torr, butene-1 75 torr. Initial pressure of pentane was 200 torr, in each case.  $T = 520^{\circ}\text{C}$ .

2. A part of the added ethylene was consumed in the first thirty minutes of the reaction, as it can be seen from curve 1 in Fig. 2.

3. The rate of product formation strongly changed; the rate of formation of butene-1, propylene and methane increased, while that of ethane and hydrogen decreased (Fig. 3).

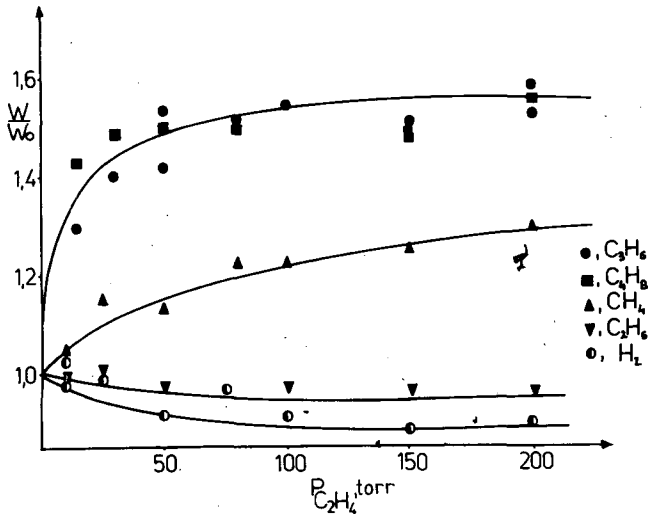


Fig. 3. Initial rate of formation of the products in the ethylene influenced reaction. Initial pressure of pentane 200 torr,  $T = 520^\circ\text{C}$ .

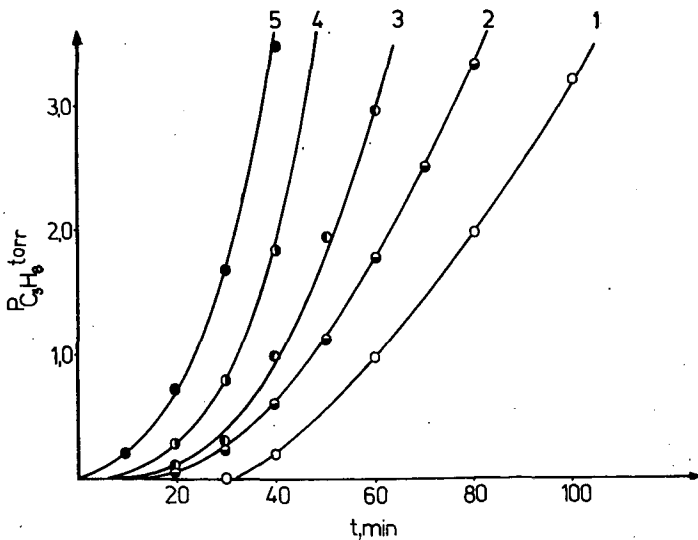


Fig. 4. Partial pressure of propane in the course of the reaction in the presence of 0 torr (1), 25 torr (2), 50 torr (3), 100 torr (4), and 200 torr (5) of ethylene.

4. In the presence of added ethylene, formation of propane was observed in the earliest part of the reaction, while without added ethylene there was an induction period in the formation of propane (Fig. 4).

*Effect of Propylene.* In the presence of added propylene the following effects have been observed:

1. Added propylene increased slightly the rate of decomposition of *n*-pentane. The effect of added propylene on the initial rate, measured manometrically, was similar to the earlier results [1, 2] (Fig. 5).

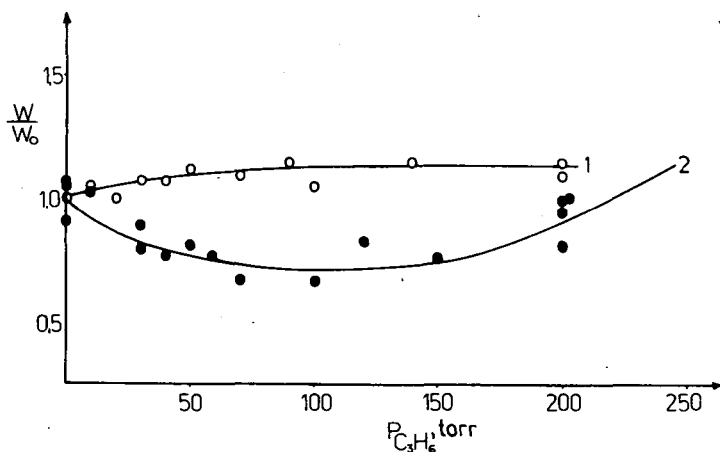


Fig. 5. Effect of added propylene on the initial rate measured by gas chromatography (1) and manometrically (2). Initial pressure of pentane 200 torr,  $T=520^{\circ}\text{C}$ .

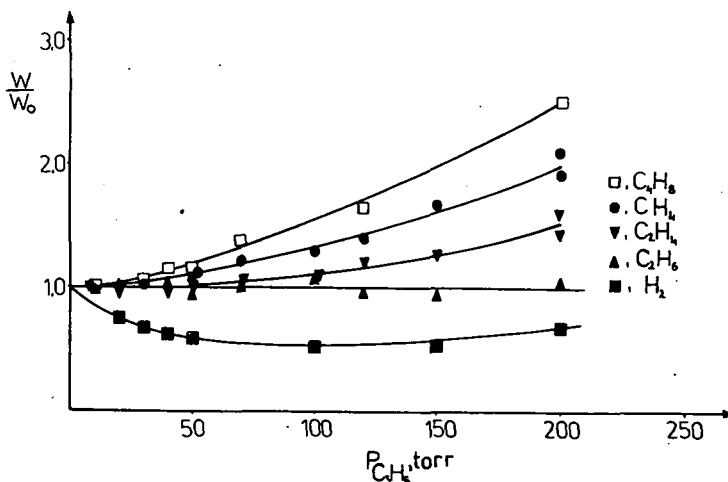


Fig. 6. Initial rates of formation of the products in the propylene influenced decomposition of pentane. Initial pressure of pentane 200 torr,  $T=520^{\circ}\text{C}$ .

- The partial pressure of added propylene was constant in time (Curve 2 in Fig. 2).
- The rate of formation of the products was strongly altered; the rate of formation of butene-1, methane, ethylene increased, while the rate of formation of ethane remained constant and that of hydrogen decreased (Fig. 6).
- In the presence of added propylene, propane was formed without an induction period. Similar observation was made in the case of added ethylene.

*Effect of Butene-1.* The effect of butene-1 can be summarised as follows:

- Added butene-1 influenced the initial rate, measured manometrically, according to a minimum curve and increased slightly the rate of decomposition of *n*-pentane measured by gas chromatography (Fig. 7).

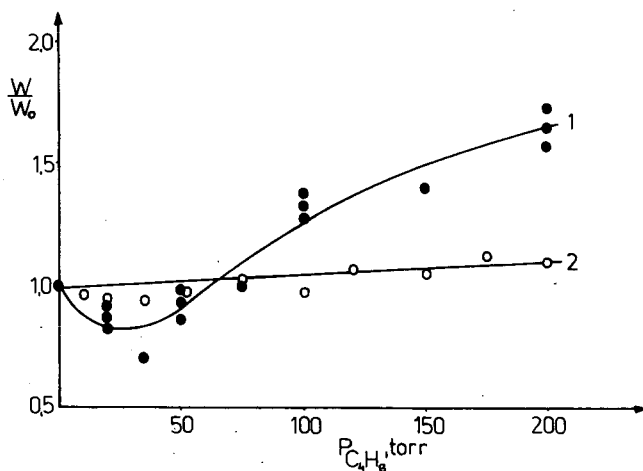


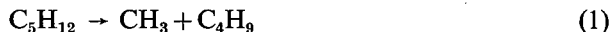
Fig. 7. Effect of butene-1 on the initial rates measured manometrically (●) and by gas chromatography (○). Initial pressure of pentane 200 torr,  $T=520^{\circ}\text{C}$ .

- Added butene-1 was consumed in the whole course of the reaction (Curve 3 in Fig. 2).
- Added butene-1 altered the rate of formation of the products. The rate of formation of methane increased with increasing amount of butene-1. The rate of formation of propylene, ethane, ethylene and hydrogen increased according to a minimum curve (Fig. 8).
- In the presence of added butene-1, propane was formed even in the earliest part of the reaction. Similar observations were made in the presence of ethylene and propylene.

#### Mechanism of the Reaction

The results can be interpreted by the following steps.

Initiation:



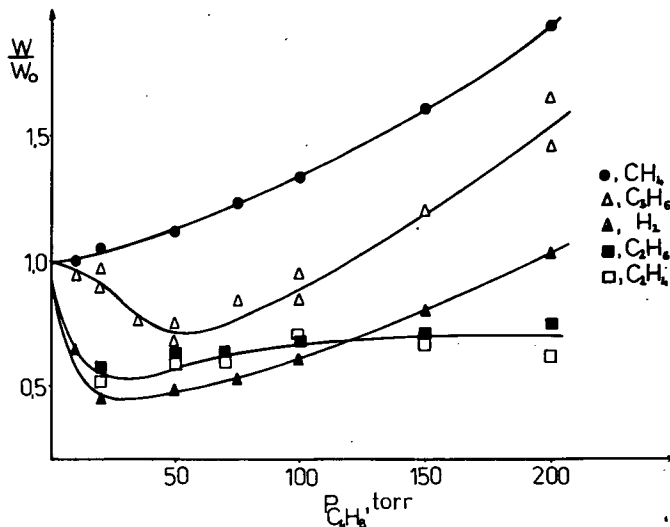
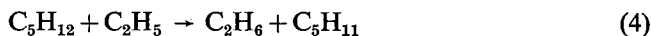
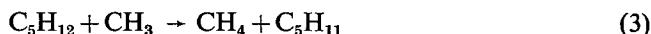
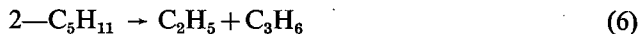


Fig. 8. Initial rates of formation of the products in the butene-1 influenced reaction.

The possibility of splitting off a hydrogen atom in the initial step can be neglected because of a greater activation energy [5]. As propane has been observed only in small quantities and butane has not been detected, methyl and ethyl radicals were accepted as the main chain carriers. This is supported by the fact that methane and ethane are major products. With methyl and ethyl radicals the following propagation steps were selected:



Pentyl radicals can reproduce the chain carriers as follows:



Among the reactions of the propyl radicals, the decomposition has the most important role [6]:



The production of hydrogen can be explained by the decomposition of alkyl radicals into an olefin molecule and a hydrogen atom:



H radical with *n*-pentane can give hydrogen:



To estimate the relative importance of the termination steps, the ratios of the concentrations of the radicals have been calculated.

In the earliest stages of the pyrolysis of *n*-pentane the following rate equations can be taken:

$$W_{H_2} = \frac{d[H_2]}{dt} = k_{H_2} [H] [\text{Pentane}]$$

$$W_{CH_4} = \frac{d[CH_4]}{dt} = k_{CH_4} [CH_3] [\text{Pentane}]$$

$$W_{C_2H_6} = \frac{d[C_2H_6]}{dt} = k_{C_2H_6} [C_2H_5] [\text{Pentane}]$$

$$W_{C_3H_8} = \frac{d[C_3H_8]}{dt} = k_{C_3H_8} [C_3H_7] [\text{Pentane}]$$

The ratios of the radicals can be expressed as follows:

$$\frac{[C_2H_5]}{[CH_3]} = \frac{W_{C_2H_6}}{W_{CH_4}} \cdot \frac{k_{H_2}}{k_{C_2H_6}}$$

$$\frac{[C_2H_5]}{[C_3H_7]} = \frac{W_{C_2H_6}}{W_{C_3H_8}} \cdot \frac{k_{C_3H_8}}{k_{C_2H_6}}$$

$$\frac{[C_2H_5]}{[H]} = \frac{W_{C_2H_6}}{W_{H_2}} \cdot \frac{k_{H_2}}{k_{C_2H_6}}$$

Table I

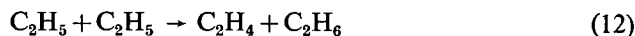
Kinetical parameters at 520°C

Reaction	Formation rate in torr <sup>-1</sup> ·min <sup>-1</sup> [4]	Rate constant in cm <sup>3</sup> ·mol <sup>-1</sup> ·sec <sup>-1</sup> [9]
H + C <sub>5</sub> H <sub>12</sub> → H <sub>2</sub> C <sub>5</sub> H <sub>11</sub>	$W_{H_2} = 0.1$	$5.1 \cdot 10^{11}$
CH <sub>3</sub> + C <sub>5</sub> H <sub>12</sub> → CH <sub>4</sub> + C <sub>5</sub> H <sub>11</sub>	$W_{CH_4} = 0.7$	$1.0 \cdot 10^9$
C <sub>2</sub> H <sub>5</sub> + C <sub>5</sub> H <sub>12</sub> → C <sub>2</sub> H <sub>6</sub> + C <sub>5</sub> H <sub>11</sub>	$W_{C_2H_6} = 0.6$	$1.04 \cdot 10^8$
C <sub>3</sub> H <sub>7</sub> + C <sub>5</sub> H <sub>12</sub> → C <sub>3</sub> H <sub>8</sub> + C <sub>5</sub> H <sub>11</sub>	$W_{C_3H_8} = 0.05$ (uncertain)	$1.04 \cdot 10^8$ (estimated)

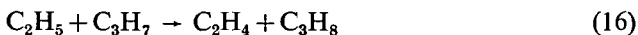
Using the values listed in Table I the following relationship has been found:

$$[C_2H_5]:[CH_3]:[C_3H_7]:[H] = 2802:340:233:1$$

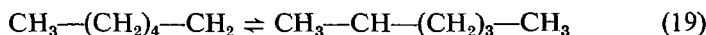
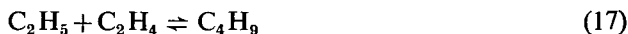
On the basis of this relationship the most important termination steps are:



Less important steps are the following:

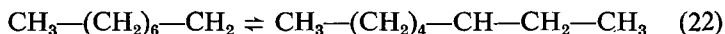
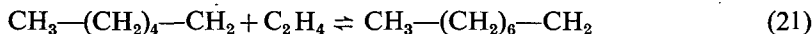


In order to interpret the increasing rate of formation of propylene, methane and butene-1 and the decreasing rate of formation of ethane and hydrogen in the presence of added ethylene, the following possible steps can be considered in accordance with literature [7, 8]:



The propyl radical produced in reaction 20 decomposes according to step 8 giving methane.

The formation of surplus butene-1, due to the addition of ethyl radical to ethylene, can be explained by the following steps:



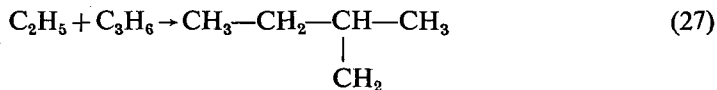
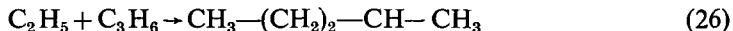
The consumption of ethyl radical in step 17 would require a decrease in ethane production. This is compensated in part by the reaction between ethylene and hydrogen atom; the decrease in the formation of hydrogen can be explained in this way:



Propyl radicals are responsible for propane formation. In the reactions influenced by ethylene there is greater opportunity to form propyl radicals in the following step as in the uninfluenced reaction.

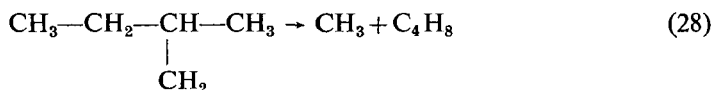


In the reaction influenced by propylene the larger amount of butene-1 can be explained by the reaction between ethyl radical and propylene. There are two ways for this reaction:





*i*-Pentyl radical can decompose in this case as follows:



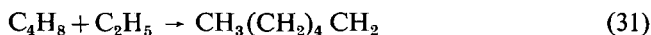
The excess amount of ethylene can be formed as follows:



The consumption of hydrogen can be understood as before.

The formation of propane in the early part of the reaction can be explained by the growing importance of propyl radical which can be formed from the relatively greater quantity of ethylene and methyl radical.

The larger amount of methane and propylene in the butene-1 influenced reaction can be interpreted as follows:



In the early stage of the reaction the formation of propane can be explained with reaction 31 (steps 19—20). In the initial rate of formation *versus* concentration of butene-1 curves the minimum can not be interpreted in a satisfactory way.

From the experimental data it can be seen that in the decomposition of *n*-pentane the olefines produced in the process have no inhibiting effect.

It seems desirable to study the effect of nitric oxide which is known as a strong inhibitor of the reaction.

#### References

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#### ТЕРМИЧЕСКОЕ РАЗЛОЖЕНИЕ *n*-ПЕНТАНА. II. ВЛИЯНИЕ НЕНАСЫЩЕННЫХ ПРОДУКТОВ И МЕХАНИЗМ РЕАКЦИИ

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Изучалось пиролиз *n*-пентана при температуре 520°C и начальных давлениях 200 мм рт. ст. при наличии этилена, пропилена и 1-бутена. В присутствии олефинов наблюдалось резкое изменение состава продуктов реакции. Эти эффекты истолкованы предположением аддиции алкильных радикалов к олефинам.