

# THERMAL DECOMPOSITION OF *n*-PENTANE. I RATE—PRESSURE RELATIONS AND SURVEY OF REACTION PRODUCTS

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The pyrolysis of *n*-pentane has been investigated at temperatures between 510 and 560 °C and at initial pressures of 50—300 torr. The reaction was followed by pressure-measurements and by gas chromatographic analysis. First-order rate constants were calculated for *n*-pentane consumption from analytical data. Initial rates were determined for the formation of products and that of *n*-pentane consumption. A stoichiometric equation for the decomposition of *n*-pentane is given.

## *Introduction*

In the investigations on the thermal decomposition of simple saturated hydrocarbons much less attention has been paid to the decomposition of pentanes than to that of the lower members of the homologue series. From the results obtained so far, the conclusion may be drawn that the mechanism of these reactions depends very much on the nature of the radicals and on that of the products formed. There is a great difference in the mechanism when, for instance, H atoms instead of alkyl radicals are the dominant chain carriers. In order to get a more detailed picture of these elementary steps, the re-investigation of the decomposition of pentanes seemed desirable.

The results of the first experiments [1, 2, 3] on the decomposition of *n*-pentane were based on pressure-change measurements and on mass spectrometric analysis.

## *Experimental*

The experiments were carried out in a conventional static system described earlier [4]. The cylindrical reaction vessel of 250 ml capacity was enclosed in an electrically heated furnace, the temperature of which was constant within  $\pm 0.3$  °C. The reaction was followed by pressure-measurements and by gas chromatographic analysis on a Carlo Erba Fr. Mod. C gas chromatograph equipped with a thermal conductivity detector. Samples were taken from the reaction vessel by means of a gas sampling valve and analysed on three columns. One of them was 0.5 cm in diameter and 170 cm in length and packed with 40—80 mesh (A.S.T.M.) molecular

sieve 5A; this column was used for the analysis of hydrogen and methane. The other column was 260 cm long, filled with 100–200 mesh alumina, and was used for the analysis of hydrocarbons up to  $C_3$  fractions. Prior to entering the alumina column, the  $C_4$  and  $C_5$  hydrocarbons were retained on a 170 cm long supplementary column filled with 30 per cent (W/W) didecyl phthalate on 70–100 mesh firebrick and kept at 0°C. The third column was 500 cm long, packed with 20 per cent didecyl phthalate, on 70–100 mesh firebrick. Helium and argon were used as carrier gas.

To make the reproducibility satisfactory, the reaction vessel was seasoned by pyrolysing 200 torr of *n*-pentane at 520°C for 72 hours.

The *n*-pentane was distilled three times at low temperatures under vacuum; after this treatment no impurities were detectable gas chromatographically. For the identification of the products, hydrogen, methane, ethane, propane, ethylene, and propylene were taken from cylinders and purified as mentioned above. Butene-1 was prepared from butanol by catalytic dehydration.

### Results and Discussion

In order to investigate the effect of initial pressure and that of temperature, experiments were carried out at 510, 520, 530, 540, 550, and 560°C and at initial pressures of 50, 100, 150, 200, 250, and 300 torr. The  $\Delta P-t$  curves are plotted in Fig. 1 and Fig. 2.

Initial rates determined from the  $\Delta P-t$  curves are shown in Fig. 3. Overall orders and activation energies were determined on the basis of initial rates. The results are listed in Table I. and are plotted in Fig. 4 and Fig. 5.

At 540°C the pressure increase was found to be 136 per cent of the initial pressure. On varying the initial pressure and temperature, no systematic change could be observed in this value.

The relation between the partial pressure of *n*-pentane determined gas chromatographically and the percentage conversion of the reaction calculated on the basis of pressure

change  $\left( \text{conversion \%} = 100 \frac{\Delta P}{\Delta P_{\infty}} \right)$  has been plotted in Fig. 6.

The consumption of *n*-pentane determined gas chromatographically and calculated on the basis of pressure change is shown in Fig. 7.

Only 85 per cent of *n*-pentane decomposed in the pyrolytic reaction. This fact cannot be explained alone by dead volume.

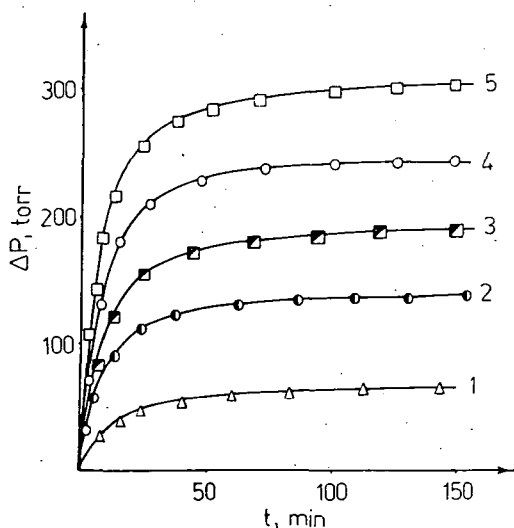


Fig. 1.  $\Delta P-t$  curves at 560°C. Initial pressures: 50 torr (1); 100 torr (2); 150 torr (3); 200 torr (4); and 250 torr (5)

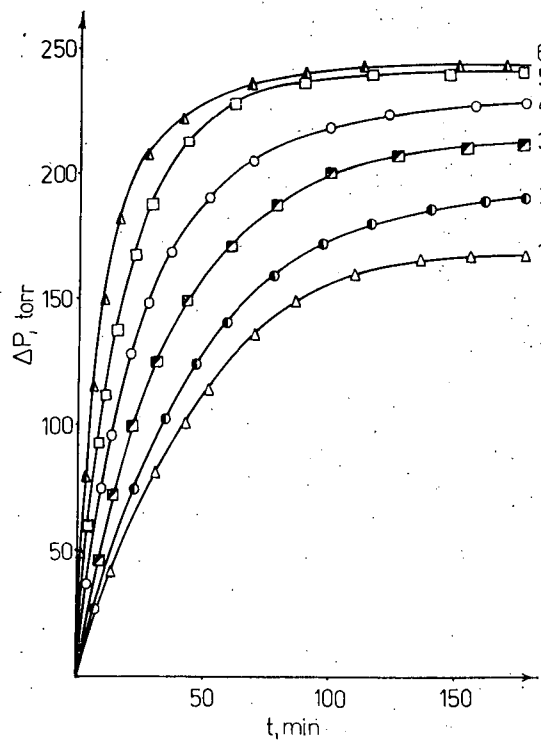


Fig. 2.  $\Delta P-t$  curves at 200 torr initial pressures at 510 °C (1); 520 °C (2); 530 °C (3); 540 °C (4); 550 °C (5); and 560 °C (6);

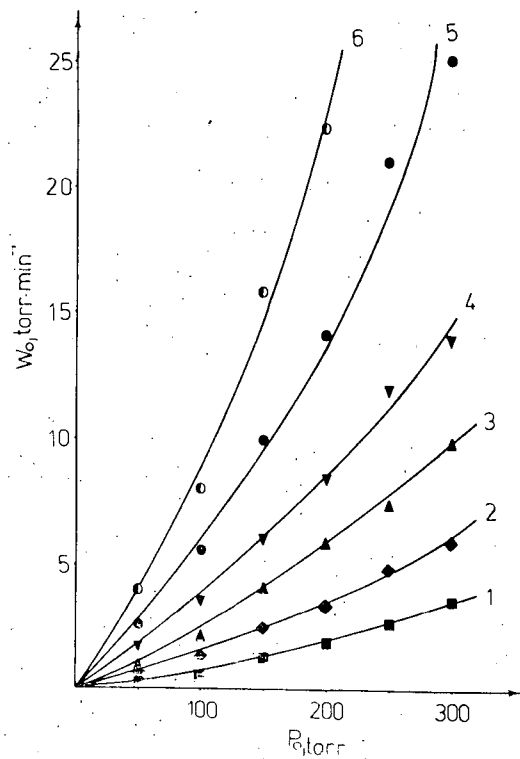


Fig. 3. Initial rates versus initial pressure at 510 °C (1); 520 °C (2); 530 °C (3); 540 °C (4); 550 °C (5); and 560 °C (6)

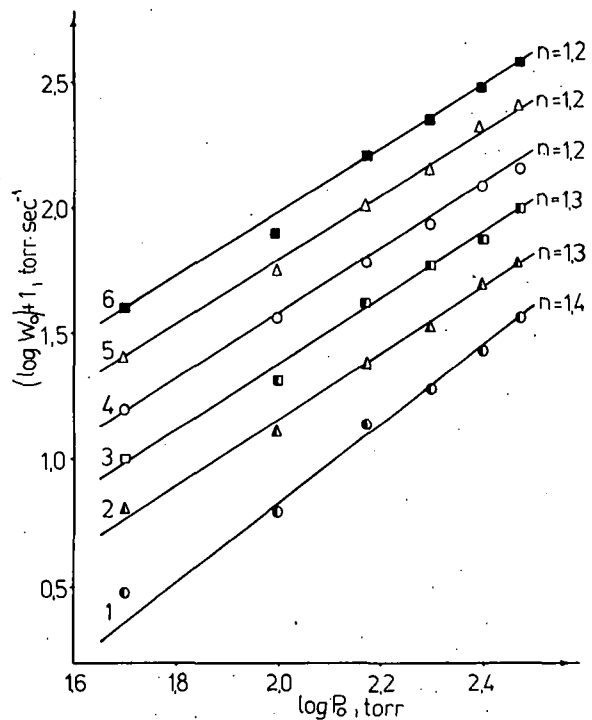


Fig. 4. Double logarithmic plot of initial rates against initial pressure at 510 °C (1); 520 °C (2); 530 °C (3); 540 °C (4); 550 °C (5); and 560 °C (6)

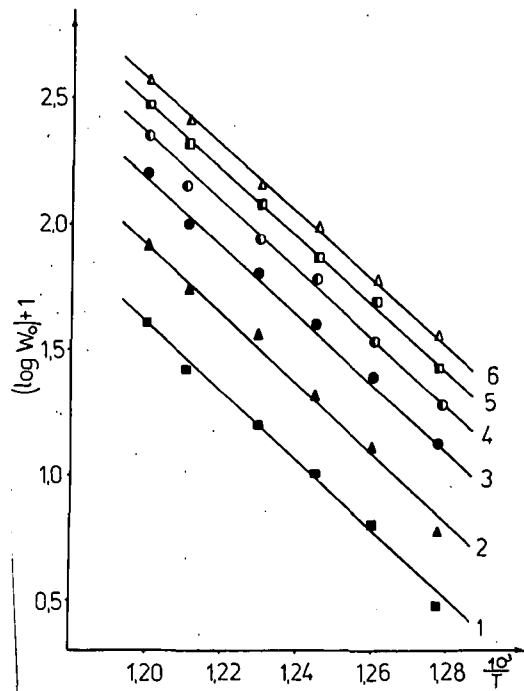


Fig. 5. Logarithm of initial rates versus reciprocal temperatures. Initial pressures: 50 torr (1); 100 torr (2); 150 torr (3); 200 torr (4); 250 torr (5); and 300 torr (6)

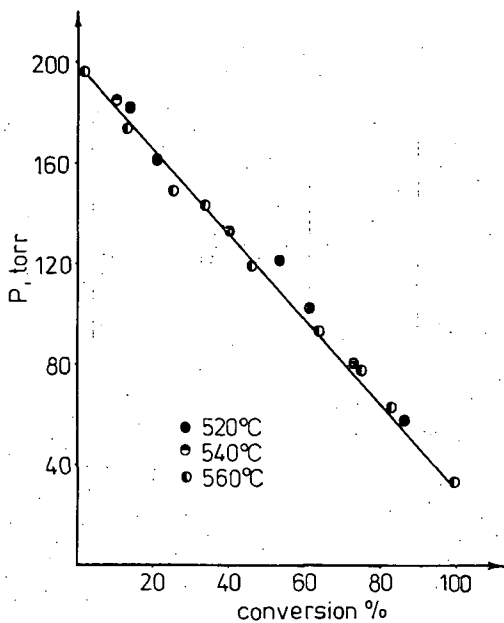


Fig. 6. Relation between partial pressure of *n*-pentane and percentage conversion. Initial *n*-pentane pressure was 200 torr. The reactions were carried out at 520, 540 and 560 °C

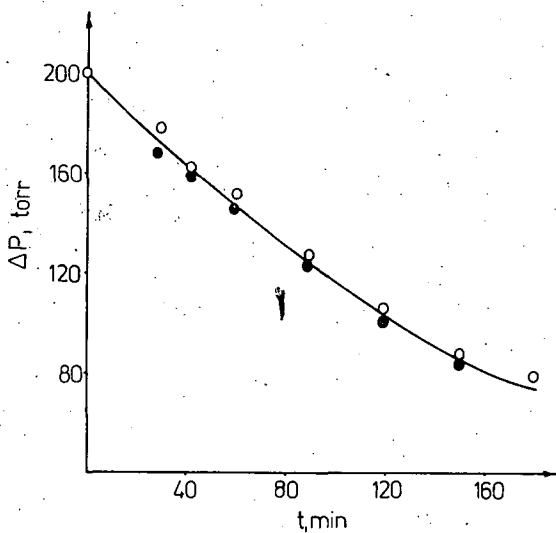


Fig. 7. Consumption of *n*-pentane determined gas chromatographically (○), and calculated from pressure change (●)

Table I

Overall activation energies at different initial pressures and overall reaction orders at different temperatures

$P_0$ torr	50	100	150	200	250	300
E kcal · mole <sup>-1</sup>	62.8	62.8	61.7	62.2 62.0*	61.7	61.7
T °C	510	520	530	540	550	560
reaction order	1.4	1.3	1.3	1.2	1.2	1.2

\* calculated from analytical results.

The products of the decomposition of *n*-pentane determined by gas chromatographic analysis were hydrogen, methane, ethane, propane, ethylene, and butene-1. Hydrogen and propane formed only in small amounts. Propane formation revealed

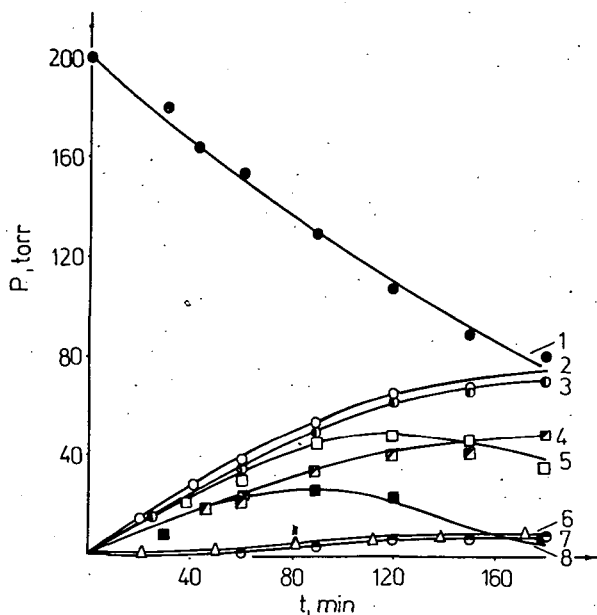


Fig. 8. Partial pressure of products versus time at 520 °C; *n*-pentane (1); methane (2); ethane (3); ethylene (4); propylene (5); hydrogen (6); propane (7); and butene-1 (8)

an induction period. Changes in the concentration of the products and in that of *n*-pentane with time have been determined and are shown in Fig. 8.

It can be seen from the figure that the concentrations of butene-1 and propylene pass through a maximum. The partial pressures of different products have been

Table II

Initial rates in torr. min<sup>-1</sup>. P<sub>0</sub> = 200 torr

Compounds	Temperature, °C		
	520	540	560
CH <sub>4</sub>	0.7	1.7	4.4
C <sub>2</sub> H <sub>6</sub>	0.6	1.5	3.5
C <sub>3</sub> H <sub>6</sub>	0.05*	0.07*	0.1*
C <sub>5</sub> H <sub>12</sub>	1.0	2.4	6.4
C <sub>2</sub> H <sub>4</sub>	0.4	1.2	3.4
C <sub>3</sub> H <sub>8</sub>	0.6	1.6	4.3
C <sub>4</sub> H <sub>8</sub>	0.4	1.6	5.1
H <sub>2</sub>	0.1*	0.2*	0.3

\* uncertain values.

Table III

First order rate constants for the thermal decomposition reaction of *n*-pentane at 520 °C and 200 torr initial pressure

t min	partial pressure of <i>n</i> -pentane	k · 10 <sup>5</sup> min <sup>-1</sup>
1	199	6.9
2	198	5.7
3	197	5.4
4	196	5.2
5	194	6.4
6	193	6.5
10	190	5.0
20	181	5.0
30	173	4.9
40	165	4.9
50	157	4.9
80	135	4.9

determined at different stages of the reaction and were plotted against conversion calculated on the basis of pressure changes (Fig. 9).

The initial rates of product formation and pentane consumption have been determined graphically from the curves obtained by plotting the partial pressure against time at 200 torr initial pressure and at different temperatures (Table II).

The reaction order for the consumption of *n*-pentane has been determined from the curve obtained by plotting the concentration against time at 520 °C and 200 torr initial pressure (Fig. 10). The reaction order for *n*-pentane consumption was found to be 1.1. First order rate constants were calculated from the analytical data. The rate constants given in Table III show a slight decreasing tendency with time.

The reaction order for the formation of ethane and ethylene was found to be 1.0, while in the case of other products it varied during the course of the reaction.

Overall stoichiometric coefficients were calculated from the ratios of the

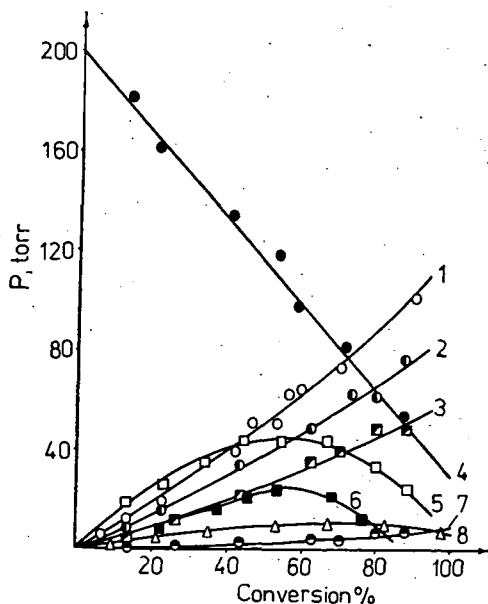


Fig. 9. Yields of the products and the reactant versus percentage conversion; methane (1); ethane (2); ethylene (3); pentane (4); propylene (5); butene-1 (6); propane (7); and hydrogen (8)

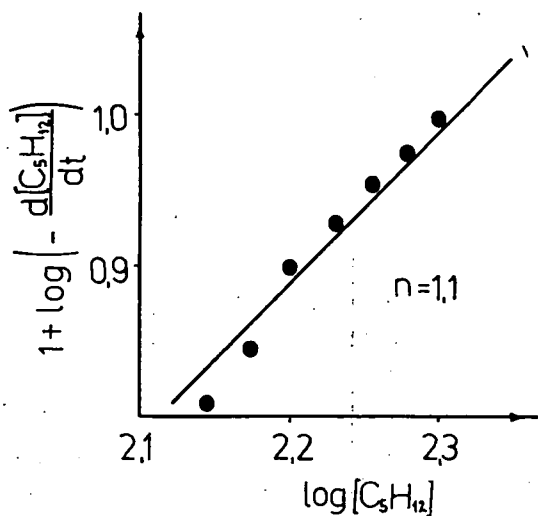


Fig. 10. Double logarithmic plot of *n*-pentane consumption rate against *n*-pentane concentration.  $P_0 = 200$  torr,  $T = 520^\circ\text{C}$

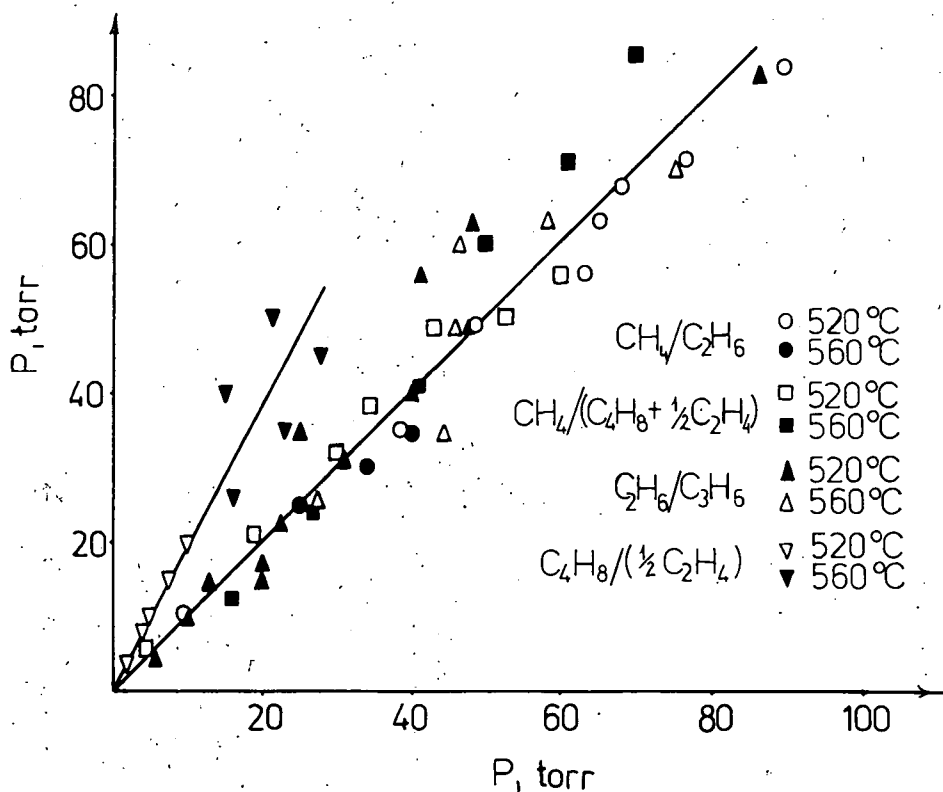


Fig. 11. The ratio of  $\text{CH}_4/\text{C}_2\text{H}_6$ ,  $\text{CH}_4/(\text{C}_4\text{H}_8 + \frac{1}{2}\text{C}_2\text{H}_4)$ ,  $\text{C}_2\text{H}_6/\text{C}_3\text{H}_6$  and  $\text{C}_4\text{H}_8/(\frac{1}{2}\text{C}_2\text{H}_4)$



products at 520 °C and 560 °C and at 200 torr initial pressure (Fig. 11). As can be seen from the figure, the values of the ratios  $C_2H_6/C_3H_6$ ,  $CH_4/C_2H_6$ , and  $CH_4/(C_4H_8 + \frac{1}{2}C_2H_4)$  are near unity and that of  $C_4H_8/(\frac{1}{2}C_2H_4)$  is equal to two. From the facts that the ratios  $CH_4/(C_4H_8 + \frac{1}{2}C_2H_4)$  and  $C_2H_6/C_3H_6$  are equal to unity, the following reaction paths can be suggested for the thermal decomposition of *n*-pentane:

- a)  $C_5H_{12} = CH_4 + C_4H_8$
- b)  $C_5H_{12} = C_2H_6 + C_3H_6$
- c)  $C_5H_{12} = CH_4 + 2 C_2H_4$

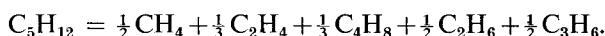
The relative importance of reactions a), b) and c) is 2:3:1, respectively. These values are based on the experimental observations that

$$C_4H_8/(\frac{1}{2}C_2H_4) \sim 2$$

and

$$CH_4/C_2H_6 \sim 1.$$

The stoichiometric equation for the decomposition of *n*-pentane can be given as follows:



The heat of reaction has been calculated on the basis of this stoichiometric equation, and was found to be 22.5 kcal/mole. The stoichiometric coefficients are only rough estimates and are valid only in the early stages of the decomposition.

There is a considerable deficit in the mass balance above 50% decomposition. This is shown in Fig. 12, where the mass balances for H and C are plotted against conversion. The  $\Delta$  values, plotted on the ordinate, were obtained as follows:

$$\Delta_C = P_{CH_4} + 2 P_{C_2H_6} + 2 P_{C_2H_4} + 3 P_{C_3H_6} + 4 P_{C_4H_8} - 5 P_{C_5H_{12} \text{ decomposed}}$$

$$\Delta_H = 4 P_{CH_4} + 6 P_{C_2H_6} + 4 P_{C_2H_4} + 6 P_{C_3H_6} + 8 P_{C_4H_8} - 12 P_{C_5H_{12} \text{ decomposed}}$$

It can be concluded from the results shown in Fig. 12, that the stoichiometry valid at low conversions does no longer describe the decomposition of *n*-pentane above about 50%. Some products of high C-atom number, not detected, must have been formed at high conversions. The H/C ratio in these products is roughly 2 (Fig. 12). The formation of higher hydrocarbons is not unexpected in the later stage of the

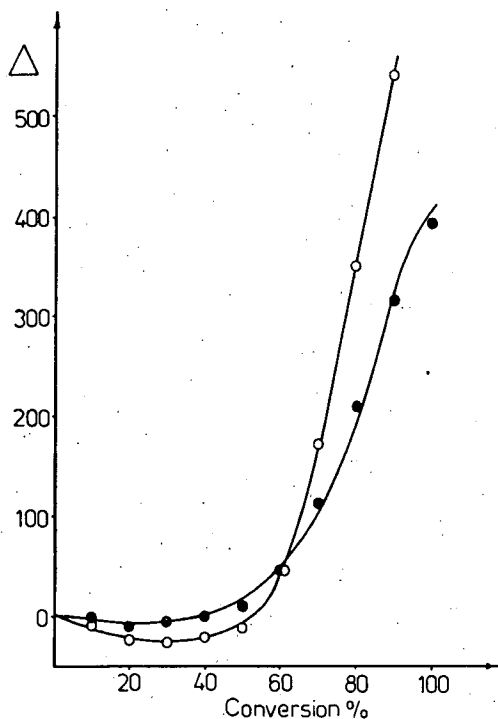


Fig. 12. Deficit of mass-balance versus percentage conversion for hydrogen (○) and carbon (●)

decomposition where the concentration of unsaturated products is high, since the free radicals are expected to add to the olefins yielding higher hydrocarbons.

Since the consumption of two products, propylene and butene-1, has been observed in the reaction, it seems desirable to carry out further investigations on the reaction in the presence of added unsaturated products of the reaction.

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#### ТЕРМИЧЕСКОЕ РАЗЛОЖЕНИЕ n-ПЕНТАНА I.

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Изучался пиролиз n-пентана при температурах от 510 до 560 °C и при начальных давлениях от 50 до 300 мм. рт. ст. За продолжением реакции следили измерением давлений и газохроматографическим анализом. На основе аналитических данные вычислены константы скорости первого порядка для расходования n-пентана. Определены начальные скорости образования продуктов и расходования n-пентана. Дано стехиометрическое уравнение реакции разложения n-пентана.