

**THERMAL DECOMPOSITION OF PROPANE IN A
RECIRCULATION SYSTEM, II.
INVESTIGATIONS IN THE ABSENCE OF OLEFIN-ABSORBER**

By

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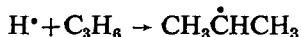
(Received 2nd June, 1982)

The pyrolysis of propane was carried out in a circulation system at four temperatures between 495 and 545 °C, with an initial propane pressure of 82 Torr, at moderate conversions. Under the given experimental conditions the ratio of methane to hydrogen (α) slightly changed with conversion and increased with temperature, in agreement with literature observations. A reaction mechanism was derived on the basis of previous experimental investigations and these experiments. The α values calculated in accordance with this mechanism are in agreement with the experimental values.

Introduction

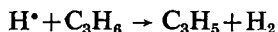
To test the recirculation system described earlier [1], propane was chosen as a model compound, because only a few, simple products are formed during its decomposition and these can easily be separated with g.c. methods. Further, the mechanism of propane decomposition is well understood, and the kinetic parameters are generally well known and reliable.

The decomposition of propane and the self-inhibition occurring in the early stages of the decomposition were investigated in detail by PURNELL AND HIS COWORKERS [2, 3]. The reaction was studied at initial pressures of 25–260 Torr, over the temperature range 450–560 °C, at low conversions, in a static system. It was established that at low conversions only five products are formed in detectable amounts. Self-inhibition was very significant in the early stages of the decomposition, and for this self-inhibition the reaction



was responsible.

According to NICLAUSE AND COWORKERS [4] and EDELSON and ALLARA [5], the reaction



also plays a significant role in the self-inhibition.

Purnell et al found that the extent of self-inhibition decreases under 500 °C and practically comes to an end under 460 °C. These experimental findings were explained in that at lower temperatures the wall-recombination of H atoms becomes more significant.

The pyrolysis of propane was investigated in great detail, over wide pressure, temperature and conversion ranges by ZALOTAI, BÉRCES and MÁRTA [6—8]; they concluded that in the thermal decomposition of propane, three different kinetic regions exist, depending on the extent and the characteristics of the olefin-inhibition, and that these regions might be characterized by different kinetic mechanism. The change in the kinetics of the decomposition is a consequence of the different reactions of the product olefins. ZALOTAI, BÉRCES AND MÁRTA stated that the kinetics of the thermal decomposition of propane

- up to 0.3% conversions follows a simple mechanism of Rice-Herzfeld type;
- at 0.3—5% conversions, the simple Rice-Herzfeld type mechanism is complemented by addition reactions of H atoms with the product olefins;
- above 5% conversions, abstraction and addition reactions of methyl radicals with the product olefins and H-atom abstraction reactions have to be considered.

The aim of this work was to test our apparatus, to acquire information on propane decomposition, and to compare our results with literature data.

Experimental

Materials

Propane. The reactant was of puriss. b. grade, supplied by Fluka. Before use it was fractionated at liquid air temperature *in vacuo*, and was stored in a glass bulb fitted with a greaseless tap.

Nitrogen. White Spot cylinder nitrogen was carefully purified and deoxygenated before use, for the decomposition is very sensitive to oxygen contamination. For deoxygenation, Catalyst BTS (Fluka) was used in a glass tube at 80 °C. The pure, oxygen-free nitrogen was stored in a glass bulb fitted with a greaseless tap.

Methane, ethane, propylene, ethylene. These compounds, which were used without further purification for calibration purposes, were supplied by MÁFKI (Hungary).

Apparatus

The decomposition reactions were carried out in an all-glass system of circulation type. The apparatus and the experimental methods used were described in detail in a preceding paper [1].

Analysis

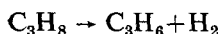
The gas-chromatographic analyses were conducted in two steps. Hydrogen was measured with a Fractovap Model C type ATC/f gas-chromatograph (Carlo Erba), equipped with a TC detector, at a column temperature of 50 °C; column: Molecular Sieve 13X, 60—80 mesh, column length 1.6 m., \varnothing 0.5 cm, carrier gas: nitrogen, flow

rate 60 cm³/min. The other products were analyzed with a Perkin-Elmer F11 apparatus; detector: FID, column: Al₂O₃+1% squalane, 60—80 mesh, column length: 4 m, Ø 0.5 cm, column temperature: 80 °C, carrier gas: nitrogen, flow rate: 36.5 cm³/min.

Experimental Results

The experiments were conducted at four different temperatures (495, 515, 535, 545 °C), at total pressure of 1 atmosphere, the partial pressure of propane in every case being 82 Torr, while the circulation rate was 12 dm³/hour. The conversion was varied in the range 0.5—18%.

During the decomposition only five products were detected: methane, ethane, ethylene, propylene and hydrogen. Except for ethane, these compounds are the main products of the decomposition of propane, and are formed in the following reactions:



It is interesting to note that NICLAUSE AND HIS COWORKERS [13] detected 13 different products in the temperature range 475—520 °C, at a propane initial pressure of 20—400 Torr, at low conversions (~1%). Besides of the four main products, *n*-butane, *iso*-butane, 2,3-dimethylbutane, 1-butane, *cis* and *trans* 2-butane, 1,5 hexadiene, 4-methyl-1-pentene were detected in small amounts.

In Fig. 1 a product distribution of a typical experiment is shown. In the early stages of the reaction (<10% conversions) the amounts of the respective pair of products (CH₄—C₂H₄, C₃H₆—H₂) are about the same. At higher conversions (>10%) this agreement does not hold. With the increase of the temperature, the rates of formation of all main products increase, as it can be seen from Figs. 2a, 2b, 2c.

The ratio of the respective pair of products

Plots of the experimentally measured $p_{\text{C}_2\text{H}_4}$ vs. p_{CH_4} and $p_{\text{C}_3\text{H}_6}$ vs. p_{H_2} values under 10% conversion yielded straight lines (see Figs. 3 and 4). The slopes of these lines are as follows:

$$\text{CH}_4/\text{C}_2\text{H}_4 = 1.026 \pm 0.022 \quad \text{and} \quad \text{C}_3\text{H}_6/\text{H}_2 = 1.055 \pm 0.042$$

These values are in agreement with those of LEATHARD and PURNELL [2]: CH₄/C₂H₄ = 1.017 and C₃H₆/H₂ = 1.028.

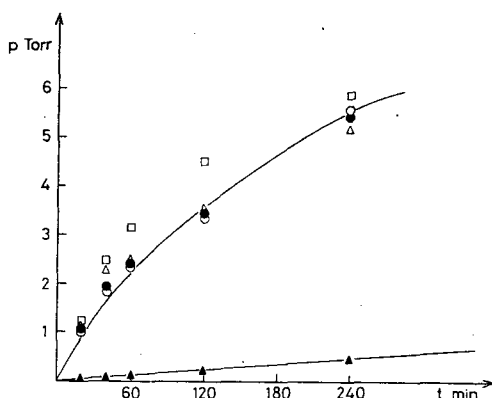


Fig. 1. Product vs time plots at 535 °C, for a propane pressure of 82 Torr. Symbols: ● C₂H₄, ○ CH₄, □ C₃H₆, △ H₂, ▲ C₂H₆. (The ethane values are multiplied by ten)

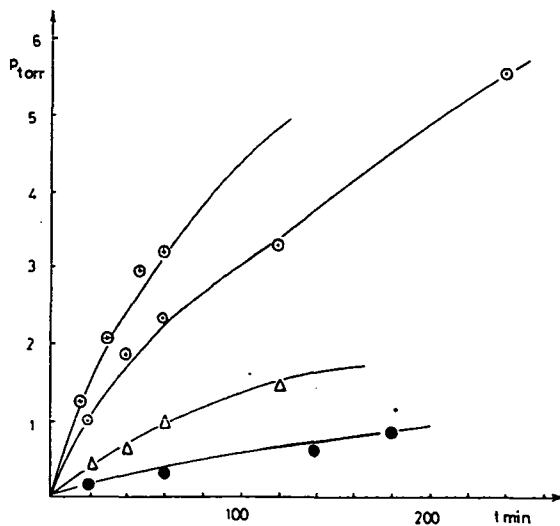


Fig. 2a. Effect of temperature on the rate of formation of methane. ● 495 °C, △ 515 °C, ○ 535 °C, ⊕ 545 °C

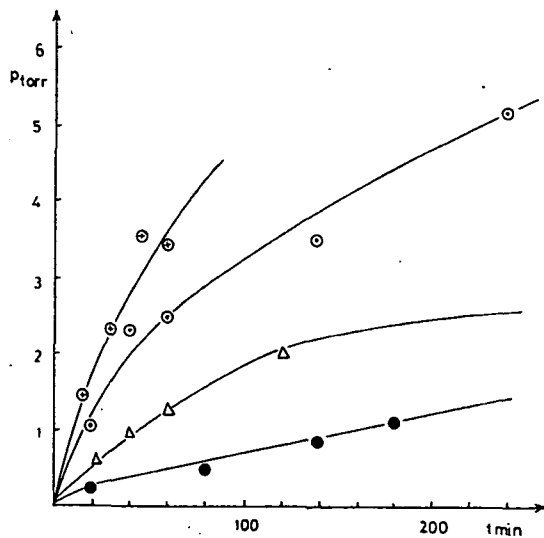


Fig. 2b. Effect of temperature on the rate of formation of hydrogen. ● 495 °C, △ 515 °C, ○ 535 °C, ⊕ 545 °C

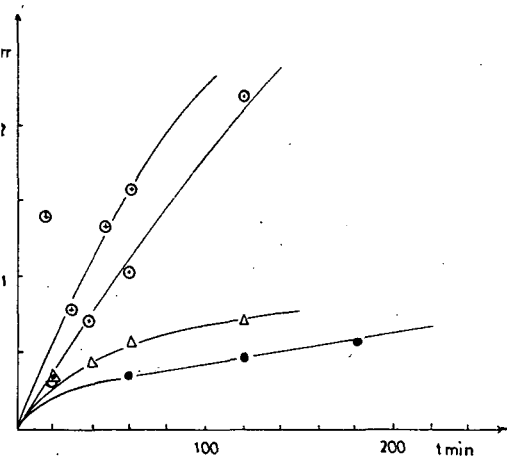


Fig. 2c. Effect of temperature on the rate of formation of ethane ● 495 °C, △ 515 °C, ○ 535 °C, ⊕ 545 °C

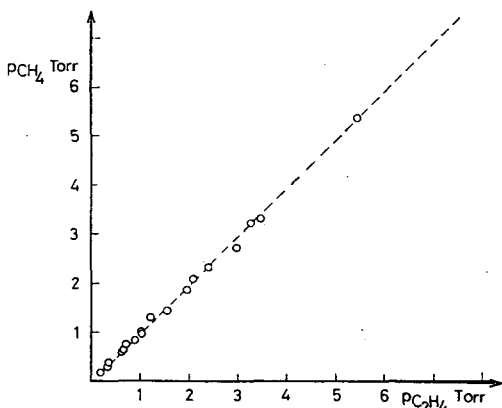


Fig. 3. Plot of methane yield against ethylene yield for 19 pyrolyses of propane, at an initial pressures of 82 Torr and temperatures in the range 495—535 °C

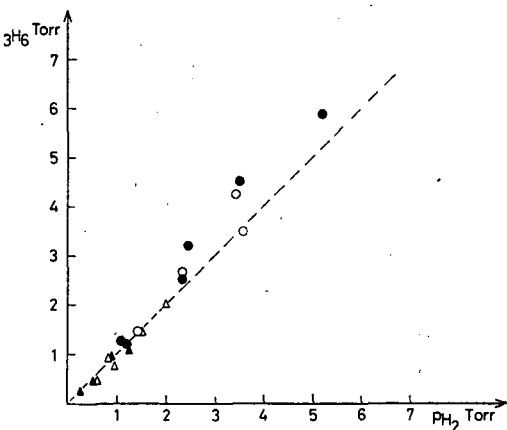


Fig. 4. Plot of propylene yield against hydrogen yield for 19 pyrolyses of propane, at initial pressures of 82 Torr and at different temperatures (▲ 495 °C, △ 515 °C, ● 535 °C, ○ 545 °C)

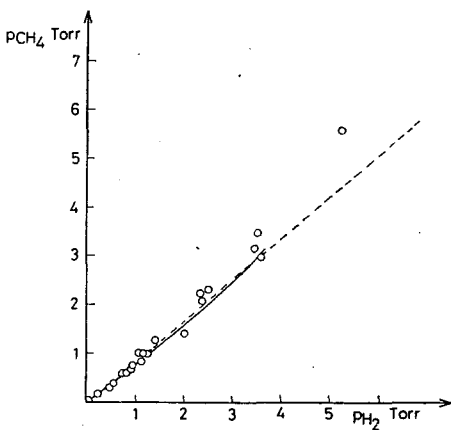


Fig. 5. Plot of methane yield against hydrogen yield for 21 pyrolyses of propane, at initial pressures of 82 Torr and temperatures in the range 495—545 °C. (The highest point was measured at 17% conversions)

The ratio of methane to hydrogen

One of the most important characteristics of propane decomposition, according to PURNELL [2], is the ratio of methane to hydrogen, which he denoted as α . In Fig. 5 the methane yield is plotted against hydrogen yield at different temperatures. It can be seen that at lower conversions (<10%) the experimental points are scattered around a straight line, but at higher conversions (>10%) the straight line inclines

towards the methane axis. The reason for this bending is that as a consequence of self-inhibition, part of the hydrogen is consumed as the decomposition proceeds. In the initial part of this curve (up to 10% conversion) it is easy to choose a linear section, the slope of which is equals 0.796 ± 0.03 . This value agrees well with that determined by LEATHARD and PURNELL [2] (0.734 ± 0.008) at 520°C and 25–209 Torr.

The ratio $\text{CH}_4/\text{H}_2 = \alpha$ increases slightly with conversion, as can be seen from Fig. 6, where the results obtained in experiments at 535°C are plotted as a function of conversion. Similar behaviour was found in the α values on the increase of temperature. Table I lists all of the CH_4/H_2 values measured at four different temperatures (for comparison, in the last row of Table I we give the data calculated from the temperature dependence of α according to LEATHARD and PURNELL [2]).

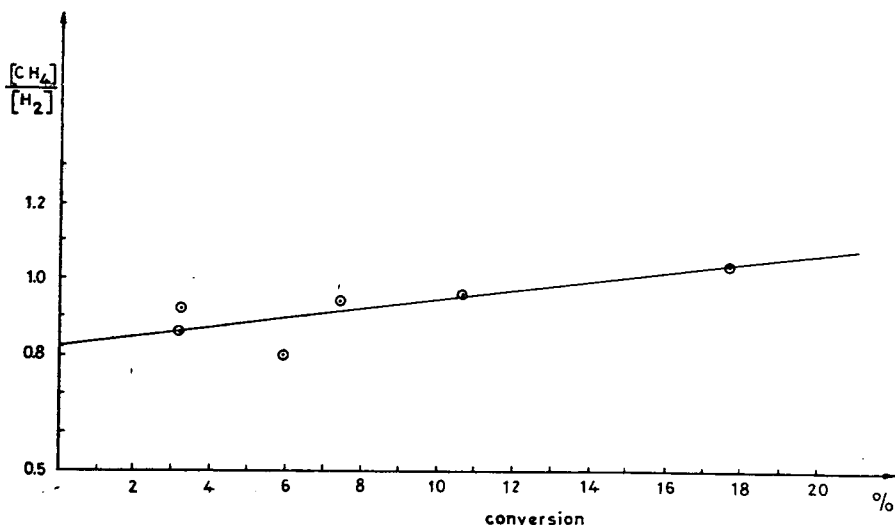


Fig. 6. Dependence of the methane-hydrogen ratio (α) on conversion, for an initial propane pressure of 82 Torr, at 535°C . The experimental points were corrected by the least square method. The intercept of the graph is α_0

Table I

Temperature-dependence of α values, measured experimentally

$t^\circ\text{C}$	495	515	535	545
$\bar{\alpha}$	0.7654	0.7968	0.8745	0.8688
α_0	0.6670	0.7304	0.8116	0.8932
α_1	(0.7039)	(0.7386)	(0.7731)	(0.7903)

$\bar{\alpha}$ denotes the mean value of α measured at these temperatures;

α_0 values were determined from the α vs. conversion plots (see Fig. 6);

α_1 values were calculated from the temperature-dependence expression for α given in [2].

Discussion

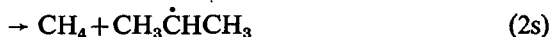
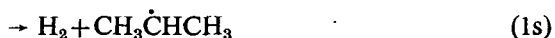
There is general agreement in the literature that the decomposition of propane is entirely free radical in nature. In the early stages of the reaction (up to 5% conversions) the decomposition can be described by the following simple mechanism:

The only important initiation reaction is

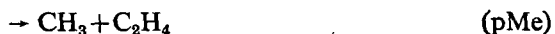


for in this temperature range other steps (such as $\text{C}_3\text{H}_8 \rightarrow \text{H} + 1-\text{C}_3\text{H}_7$ or $\text{C}_3\text{H}_8 \rightarrow \text{H} + 2-\text{C}_3\text{H}_7$) are negligible [2, 8].

This initiation reaction is followed by the following H atom transfer reactions:



During the decomposition of the *n* and *sec*-propyl radicals:



ethylene and propylene are formed. From the known rate coefficients it is easy to calculate that reaction (pH) is negligible compared to reaction (pMe) under our experimental conditions. (The ratio of rate constants $\text{pMe/pH} = 43.26$ at 495°C and 33.87 at 545°C . The two routes of *sec*-propyl decomposition, (sMe) and (sH), play equally important roles (the ratio of rate constants $\text{sH/sMe} = 5$ at 495°C).

The ethyl radicals formed during the decomposition of propane take part in H atom abstraction reactions



and form ethane. At the temperatures of our experiments, the decomposition of the ethyl radical



is also important.

During the early decomposition the self-inhibition plays a significant role, so the following addition reactions between H atoms and product olefins are very im-

portant:



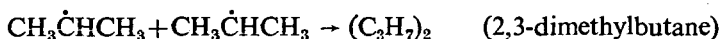
At very low conversions, the only chain termination step is the methyl radical recombination



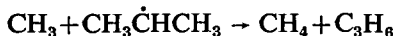
but at higher conversions the reactions



and



take part too. These latter products were detected by NICLAUSE AND COWORKERS [4]. Other possible termination steps are



From the mechanism described above, according to the deduction of ZALOTAI, BÉRCES and MÁRTA [6], the following expression can be given for the ratio CH_4/H_2 :

$$\frac{[\text{CH}_4]}{[\text{H}_2]} = \frac{k_2 [\text{Me}]}{k_1 [\text{H}]}$$

where

$$\frac{k_2}{k_1} = \frac{k_{2p} + k_{2s}}{k_{1p} + k_{1s}}$$

and

$$\frac{[\text{Me}]}{[\text{H}]} = \frac{2 \frac{k_1}{k_{-H}} [\text{C}_3\text{H}_8] + 2[\text{C}_3\text{H}_6] + (1 - \gamma)[\text{C}_2\text{H}_4]}{2 \frac{k_2}{k_{-H}} \beta [\text{C}_3\text{H}_8]}$$

while

$$\beta = \frac{k_{sH} + \alpha' k_{pH}}{k_{sMe} + \alpha' k_{pMe}} \quad \text{and} \quad \alpha' = \frac{k_{sH} + k_{sMe}}{k_{pH} + k_{pMe}}$$

$$\gamma = \frac{k_{eH}}{k_{eH} + 2k_3[\text{C}_3\text{H}_8]}$$

$$k_3 = \frac{k_{3p} + k_{3s}}{2}$$

$$k_{-H} = k_{p-H} \approx k_{s-H}$$

Using this expression, we calculated the values which are given in the fifth column of Table II. The Arrhenius parameters used in these calculations are shown in Table III. As our mechanism is valid only for 5% conversions, Table II includes only those experimental data which were within this conversion range.

As can be seen from Table II, the calculated data are different from the experimental data by a factor of two, but the tendency of α to change with conversion is

Table II
Measured and calculated α values at different temperatures

t °C	No.	Conversion %	α experimental	α calculated (ZBM)	α calculated (LP)
495	166	0.552	0.7100	1.4725	0.6644
	167	1.049	0.6960	1.4903	0.6728
	171	1.124	0.6554	1.4895	0.6738
	168	1.946	0.7193	1.5319	0.6803
	169	2.68	0.7473	1.5557	0.6852
515	198	1.262	0.7073	1.6608	0.6811
	181	2.107	0.7081	1.6830	0.6868
	219	2.371	0.7795	1.6496	0.6874
	182	3.096	0.7781	1.7470	0.6924
	183	4.5159	0.7105	1.8029	0.7061
535	194	3.202	0.9202	1.7606	0.7012
	225	3.218	0.8569	1.7718	0.7044
545	215	4.053	0.9025	1.7711	0.7015

(ZBM) α values calculated with the expression given by Zalotai, Bérces and Márta.

(LP) α values calculated with the expression given by Leathard and Purnell.

Table III
Propane decomposition rate parameters used in our calculations

Reaction	$\log A$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	E_a kcal/mole	References
$\text{H} + \text{C}_3\text{H}_8 = \text{H}_2 + \text{P}^\cdot$	11.1	9.7	[11]
$= \text{H}_2 + \text{S}^\cdot$	10.8	7.7	[11]
$\text{CH}_3 + \text{C}_3\text{H}_8 = \text{CH}_4 + \text{P}^\cdot$	9	11.5	[12]
$= \text{CH}_4 + \text{S}^\cdot$	8.8	10.5	[11]
$\text{P}^\cdot = \text{H}^\cdot + \text{C}_2\text{H}_6$	13.2	38.6	[11]
$= \text{CH}_3 + \text{C}_2\text{H}_5$	13.1	32.5	[11]
$\text{S}^\cdot = \text{H}^\cdot + \text{C}_2\text{H}_6$	13.9	40.4	[11]
$= \text{CH}_3 + \text{C}_2\text{H}_5$	14.6	44	[13]
$\text{C}_2\text{H}_5 + \text{C}_3\text{H}_8 = \text{C}_2\text{H}_6 + \text{P}^\cdot$	8.5	12.3	[11]
$= \text{C}_2\text{H}_6 + \text{S}^\cdot$	7.7	10.4	[11]
$\text{C}_2\text{H}_5 = \text{C}_2\text{H}_4 + \text{H}^\cdot$	13.6	40.5	[11]
$\text{H} + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_5$	10.6	2.6	[11]
$\text{H} + \text{C}_3\text{H}_8 = \text{P}^\cdot$	9.9	2.9	[14]
$= \text{S}^\cdot$	9.9	1.2	[14]

the same in each case. The cause of the difference between the two sorts of data may originate from the inaccuracy of the Arrhenius parameters used during the calculations, and/or the simple mechanism for the decomposition of propane needs some correction.

It can be seen from Table II that the tendency of α to change with conversion is better at higher than at lower temperatures, so the difference between the experimental and calculated α values decreases with the increase of temperature.

According to LEATHARD and PURNELL [2], at low conversions ($\sim 2\%$) the following simple expression can be given for the ratio of methane to hydrogen:

$$\frac{[\text{CH}_4]}{[\text{H}_2]} = \frac{1 + k_{2p}/k_{2s}}{1 + k_{1s}/k_{1p}} \left\{ \frac{1 + k_{p-H}[\text{H}_2]}{2k_{1s}[\text{C}_3\text{H}_8]} \right\}$$

Using this formula, we calculated the α values which are to be found in the sixth column of Table II. From these data it can be seen that at 495 and 515 °C, at low conversions ($< 2\%$), there is good agreement between the experimental and calculated values. With the increase of temperature and conversion a significant negative error appears. This fact shows that with increasing conversion, not only reaction steps (p-H) and (s-H), but also other inhibition steps play a dominant role.

The above data verify the fact that, under 5% conversions, this simple mechanism describes the decomposition of propane moderately well in our circulation system too. The results of our investigation permit the continuation of experiments on propane decomposition in this system using the olefin-absorber.

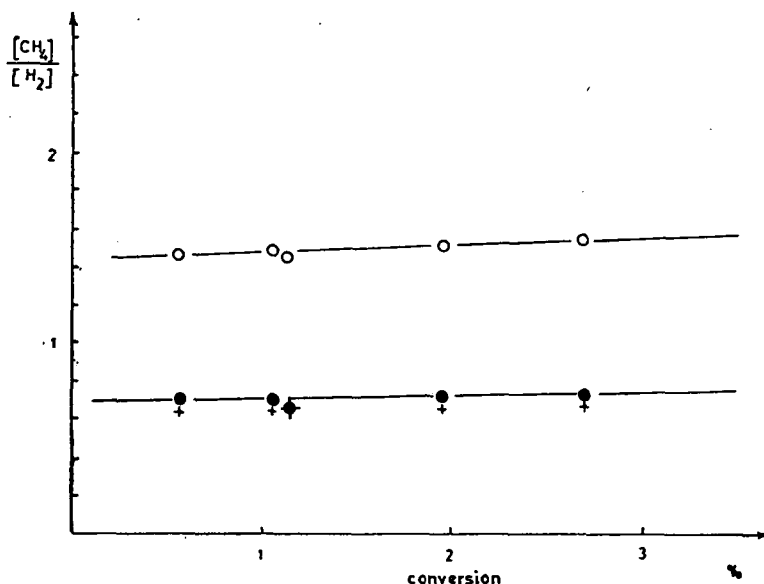


Fig. 7. Dependence of the methane-hydrogen ratio on conversion, for an initial propane pressure of 82 Torr: ● experimental points, ○ points calculated with the expression of Zalotai, Bérces, Márta; + points calculated with the expression of Leathard and Purnell. Temperature: 495 °C

Acknowledgements

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ТЕРМИЧЕСКИЙ РАСПАД ПРОПАНА В РЕЦИРКУЛЯЦИОННОЙ СИСТЕМЕ II.
ИССЛЕДОВАНИЕ ПИРОЛИЗА В ОТСУТСТВИИ ОЛЕФИНАБСОРБЕРА

И. Барди, Т. Берцеш

Изучен термический распад пропана при температуре 495—545 °С при начальном давлении 82 тор в условиях умеренной конверсии. Соотношение метана к водороду (α) в небольшой степени зависит от конверсии и растёт с повышением температуры. На основании экспериментальных данных написан простой механизм превращения. Значения α , рассчитанные по механизму, близки к значениям экспериментов.