

THERMAL DECOMPOSITION OF PROPANE IN A RECIRCULATION SYSTEM III. INVESTIGATIONS IN THE PRESENCE OF OLEFIN-ABSORBER

By

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(Received 10th October, 1982)

The pyrolysis of propane was carried out in a circulation system, in the presence of olefin-absorber, at temperatures in the range 450–545 °C, at propane pressures of 30–470 Torr, in a wide conversion range (0.1–72%). Under the given experimental conditions the ratio of methane to hydrogen (α) does not change with conversion; α increases slightly with temperature. The dependence of α on the propane concentration is a function of temperature. A simple reaction mechanism was derived on the basis of data found in the literature and from the present experimental results. The α values calculated in accordance with this mechanism are in agreement with the experimental values.

We have previously reported [1] results on the thermal decomposition of propane in a recirculation system, using a stirred flow reactor. Under these circumstances the mechanism of thermal decomposition of propane is rather complicated. The complication (the self-inhibition character of the reaction) is caused by the reactions of the product olefins. In this work we investigate the thermal decomposition of propane under olefin-free circumstances, the product olefins being removed continuously from the recirculation system with an absorber. It is to be expected that a simple mechanism is valid under olefin-free circumstances and in this way an opportunity arises to determine more exact and reliable kinetic characteristics for the thermal decomposition of propane.

Experimental

The mercury perchlorate — perchloric acid system (MP—PA) showed the best olefin-absorption capacity, and was used in our experiments. The compound was absorbed in a g.c. support, which was filled into a glass U-tube. The absorber was used at room temperature (see [1]).

The apparatus, the experimental methods and the chemicals used were described in detail in [1, 2].

The experiments were conducted at 6 different temperatures (450, 475, 495, 515, 535 and 545 °C), at a total pressure of 1 atm, the partial pressure of propane varying

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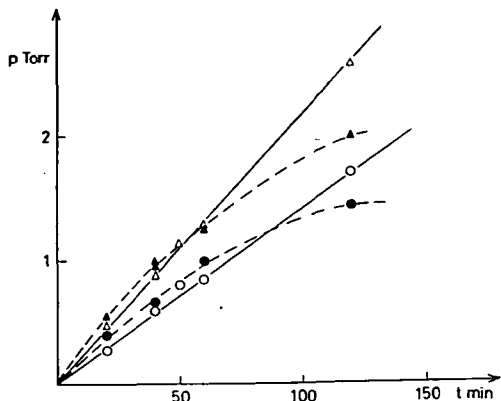


Fig. 1. Product vs. time plots at 515 °C, at a propane pressure of 61 Torr. Symbols: open triangles H_2 , open circles CH_4 (using olefin-absorber), filled triangles H_2 , filled circles CH_4 (without olefin-absorber).

pressure of 61 Torr. In the experiments in which absorber was used, the product vs. time plots give practically straight lines. As can be seen in Fig. 1, in absorber-free experiments the product vs. time plots exhibit curvature; this originates from the inhibiting effect of the product olefins.

We have earlier discussed [1] that, owing to the olefin-absorber used in the experiments, self-inhibition-free pyrolysis conditions were achieved only at 515 °C and lower temperatures, at low (<5%) conversions. At higher temperatures 535–545 °C) ethylene and propylene were detected in small amounts among the products. This was a consequence of the unsatisfactory functioning of our absorber. In the experiments conducted at temperatures higher than 515 °C, there is a definite residual olefin level; this level decreases slightly with conversion. In Fig. 2 we show the residual olefin level as a function of conversion at two temperatures. The decreasing tendency is readily observable. It is easy to explain the decrease in the concentration of olefins. The absorption of olefins in the absorber is relatively slow. For this reason, at low conversions, where as a consequence of the greater concentration of propane the rate of formation of olefins is higher, a higher stationary residual olefin level results. This level will decrease, the lower the rate of formation of olefins.

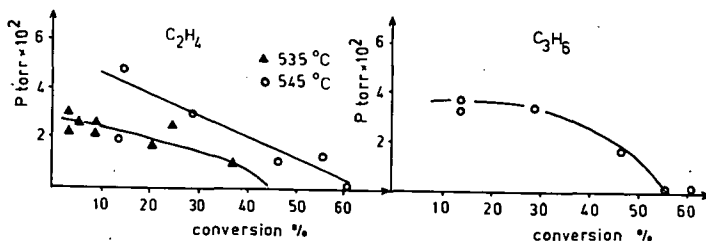


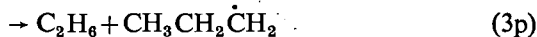
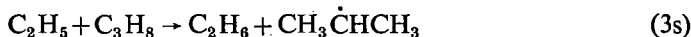
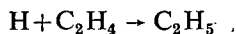
Fig. 2. Variation of residual olefin level with conversion

between 30 and 470 Torr. As diluent, carefully purified (deoxygenated) nitrogen was used. The circulation rate in every case was 12 dm³/hour. The conversion varied in the range 0.1–72%; it was calculated from the measured concentrations of products. Under the above experimental conditions, usually only three products were detected: methane, ethane and ethylene.

At 515 °C and lower temperatures the kinetics of the decomposition of propane was studied under practically olefin-free circumstances. This situation is shown in Fig. 1, which depicts the methane and hydrogen product distribution curves at 515 °C and at a propane

At 545 °C (the highest temperature in our study) it can easily be seen from the product distribution data that the amount of residual ethylene is about 0.1–1% of the methane formed, which corresponds to the concentrations formed at conversions of about 0.02–0.2% propane. In our experience, at such low conversions under our experimental conditions, self-inhibition is not yet significant. This is verified by the experimental finding that the shapes of the product formation curves for methane and hydrogen at 535 and 545 °C are similar to those obtained at lower temperatures (515, 495 °C) where there is practically no self-inhibition.

A significant difference was obtained in the ethane *vs.* conversion curves. In the olefin-absorber-free experiments, the concentration of ethane increases steeply with conversion, while in the experiments in which absorber was used, the amount of ethane changes only slightly in wide conversion and temperature ranges. At the same initial concentration of propane, more ethane is formed in the absorber-free experiments than in the presence of the absorber, and the difference increases with conversion (see Table I). This shows that in the experiments in the absence of absorber, an important ethane-producing process is the addition of an H atom to ethylene and, following this, the H atom abstraction reaction between ethyl radical and propane



Further, in the presence of olefin-absorber the nature of the chain rupture step probably changes too.

Table I

Partial pressure of ethane, measured during the
pyrolysis of propane
 $t = 535^\circ\text{C}$ $p_0 = 61$ Torr

No.	conversion %	ethane Torr
experiments with olefin-absorber		
189	3.40	0.0305
222	3.97	0.0113
190	6.09	0.0154
217	9.50	0.0144
191	9.70	0.0212
192	17.19	0.0289
193	25.25	0.0504
196	37.23	0.0333
olefin-absorber-free experiments		
194	3.20	0.0452
221	3.22	0.0216
186	5.92	0.0535
186	7.4	0.0780
187	10.61	0.1625
197	17.71	0.3582

Temperature-dependence of the main products

There is a slight temperature-dependence of the formation of methane and hydrogen in the presence of olefin-absorber, as can be seen in Fig. 3, where the pressures of CH_4 and H_2 are plotted against conversion at four different temperatures and at a propane pressure of 61 Torr. The experimental values fit a straight line, even at high conversions.

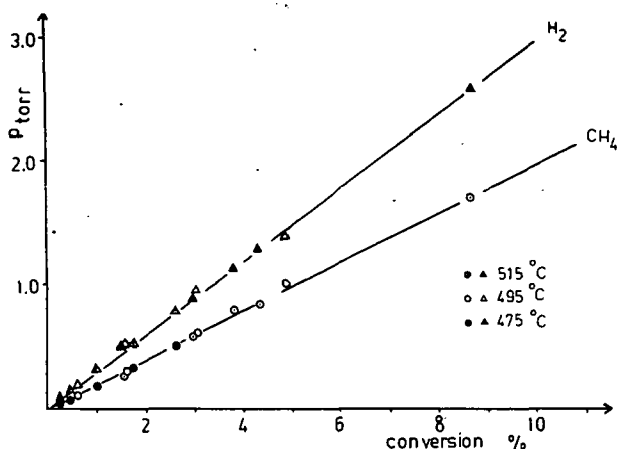


Fig. 3. Plots of hydrogen and methane yields against conversion at different temperatures (using olefin-absorber).

The ratio of methane to hydrogen

Plots of the methane pressure against the hydrogen pressure in experiments at five different temperatures and various conversions (0.01–77%) and at a propane concentration of 61 Torr yielded straight lines of slope 0.730 ± 0.0095 (Fig. 4). To simplify comparison, the same Figure gives the methane *vs.* hydrogen values obtained in olefin-absorber-free experiments under the same experimental conditions. It can be seen from Fig. 4 that at lower conversions (<10%) the two graphs coincide, but at higher conversions (>10%) the points for the absorber-free experiments deviate from linearity, the curve inclining towards the methane axis. This behaviour can be explained by the hydrogen consumption taking place as a consequence of self-inhibition. In the absorber-free experiments, the initial slope of the curve is 0.796. This value is in accordance with the slope in the presence of olefin-absorber.

The ratio of methane to hydrogen (α) shows no significant dependence on conversion, in contrast with the results of the absorber-free experiments. This can be seen in Fig. 5, where the α values obtained at 535 °C at a propane pressure of 61 Torr are plotted *vs.* conversion. For comparison, the α values obtained in absorber-free experiments are also plotted in the same Figure. It is important to note that values extrapolated to zero conversion (from experiments using olefin-absorber) are in good agreement with the α values determined directly by experiment.

Interesting behaviour was found in the dependence of α on the initial pressure of propane (see Table II and Fig. 6). In Fig. 6 the α values obtained in the presence of olefin-absorber are plotted as a function of propane pressure at 450 and 515 °C. There is a slight increase in α at 515 °C, while at 450 °C α increases significantly with increasing propane concentration. This behaviour is in agreement with literature experience [3]. For the concentration-dependence of α , the following simple expression

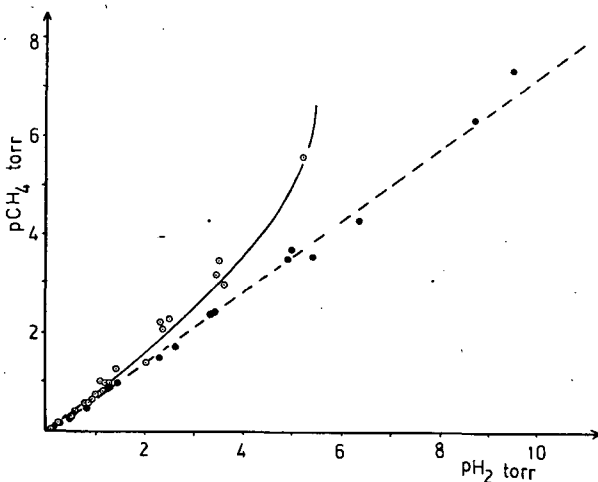


Fig. 4. Plots of methane yield against hydrogen yield in the pyrolysis of propane, at an initial pressure of 62 Torr and temperatures between 475 and 545 °C (the highest point was measured at 33.4% conversion) ● absorber-free experiments, ○ using olefin-absorber.

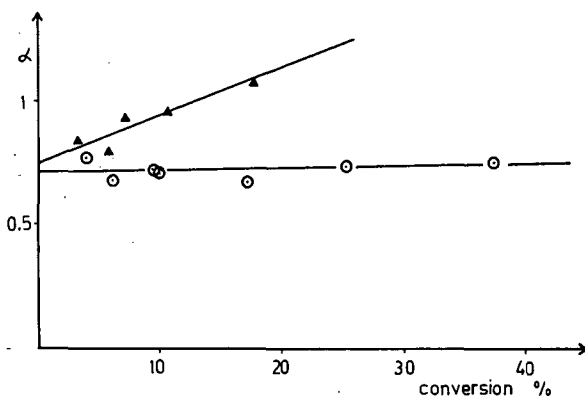


Fig. 5. Dependence of α on conversion, at an initial propane pressure of 61 Torr, at 535 °C. Open circles: using olefin-absorber, filled triangles: without olefin-absorber.

Table II
 Dependence of α on the propane pressure in the
 presence of olefin-absorber
 $t = 515^\circ\text{C}$

No.	propane Torr	conversion %	α
228	30.72	2.77	0.681
226	30.79	4.32	0.669
227	30.65	7.95	0.714
177	61.14	1.09	0.563
178	61.05	2.35	0.665
179	60.44	3.41	0.658
220	60.63	3.20	0.701
240	61.10	3.45	0.687
180	61.05	6.87	0.660
223	122.54	1.86	0.788
235	121.81	1.30	0.744
224	121.25	4.96	0.803
225	121.63	7.52	0.820
229	184.66	1.54	0.824
230	182.34	3.03	0.831
231	182.88	4.57	0.791
232	462.42	1.42	0.928
233	464.18	2.83	0.929
234	461.31	4.28	0.915

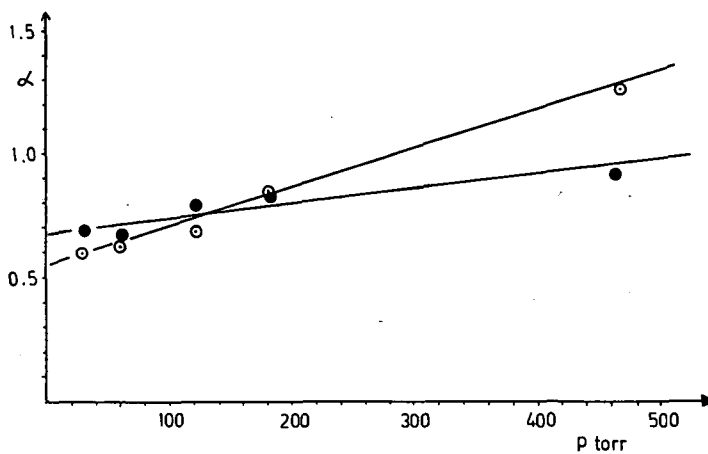


Fig. 6. Dependence of α on propane pressure at different temperatures. Filled circles: $t = 515^\circ\text{C}$, open circles: $t = 450^\circ\text{C}$.

was described by LEATHARD and PURNELL [3]:

$$\alpha = a + bp_i$$

where a and b are constants and p_i the initial pressure of propane.

From our experimental data it was possible to calculate the a and b values, which are as follows:

$$\begin{array}{ll} t = 450^\circ\text{C} & t = 515^\circ\text{C} \\ a = 0.539 \pm 0.020 & a = 0.683 \pm 0.029 \\ b = 0.0016 \pm 0.0001 & b = 0.0006 \pm 0.0001 \end{array}$$

These parameters are in approximate agreement with literature data [3].

The trend of the temperature-dependence of α is the same in the absorber-free experiments and in the experiments in the presence of olefin-absorber, *viz.* there is a slight increase in α as the temperature increases (see Table III). From our experimental

Table III

Temperature-dependence of α in the presence of olefin-absorber
 $p = 61$ Torr propane

t °C	450	475	495	515	535	545
$\bar{\alpha}$	0.631	0.619	0.657	0.671	0.720	0.728
α_0	—	0.578	0.618	0.688	0.711	0.716

$\bar{\alpha}$ = mean value of all α values measured in a system containing olefin-absorber
 α_0 = α values extrapolated to zero conversion using the α vs. conversion plots

results, the temperature-dependence of α (at a propane pressure of 61 Torr) can be described by the following expression:

$$\alpha = 10^{2.50 \pm 1.31} \exp(-2029 \pm 412/RT)$$

For comparison, PURNELL and LEATHARD [3] report that in the ranges 510—560 °C and 25—260 Torr propane the temperature-dependence of α can be described by the following expression:

$$\alpha = 10^{0.67 \pm 0.13} \exp(-2890/RT)$$

The order of reaction

From the $\log w_0$ vs. $\log p_0$ plots (where w_0 is the initial rate calculated from experiments in the presence of olefin-absorber, and p_0 is the initial pressure of propane), it was possible to determine the orders of formation of methane and hydrogen. As can be seen from Figs. 7a, 7b and 7c, similarly as for the results of LAIDLER ET AL. [4] and ZALOTAI, BÉRCES and MÁRTA [5], these plots do not give straight lines. At 515 °C the inflexion point can be found at a propane pressure of 120 Torr. The ini-

tial order of methane formation in the pressure range 120—460 Torr is 0.94, while in the range 30—120 Torr the order is 1.21. According to LAIDLER and his coworkers, first-order kinetics hold for the decomposition of propane above the inflexion point, while below the inflexion point the order is 1.5. Roughly the same order values were obtained for hydrogen formation. At 450 °C the $\log w_0$ vs. $\log p_0$ plots give practically straight lines and the initial order for methane formation is 1.21 in this case.

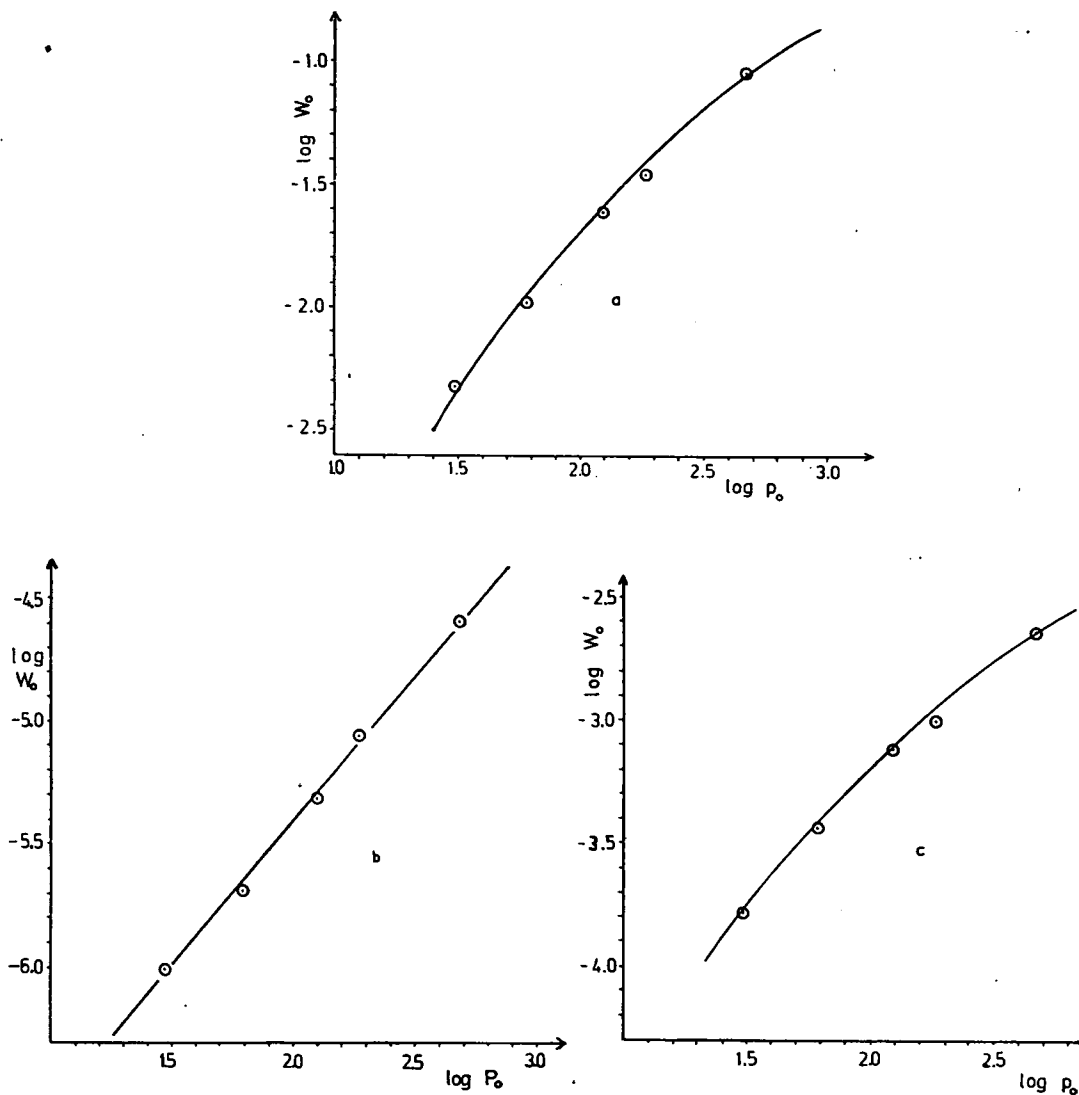


Fig. 7. $\log w_0$ vs. $\log p_0$ plots for methane and hydrogen at different temperatures. (a) $t = 515^\circ\text{C}$, CH_4 , (b) $t = 450^\circ\text{C}$, CH_4 , (c) $t = 515^\circ\text{C}$, hydrogen.

Energy of activation

From the temperature-dependence of the initial rate of formation of methane and hydrogen, the activation energy for the decomposition of propane can be determined (Fig. 8). From the $\log w_0$ vs. $1/T$ plots (using the experimental data calculated from the experiments in the presence of absorber), the following Arrhenius parameters were calculated:

$$E_a = 68.9 \pm 2.6 \text{ kcal/mol} \quad \log A = 17.2 \pm 0.7 \quad (\text{CH}_4)$$

$$E_a = 68.6 \pm 0.9 \text{ kcal/mol} \quad \log A = 16.7 \pm 0.2 \quad (\text{H}_2)$$

These values are in good agreement with data in the literature (68.0 kcal/mol in the pressure range 50—200 Torr).

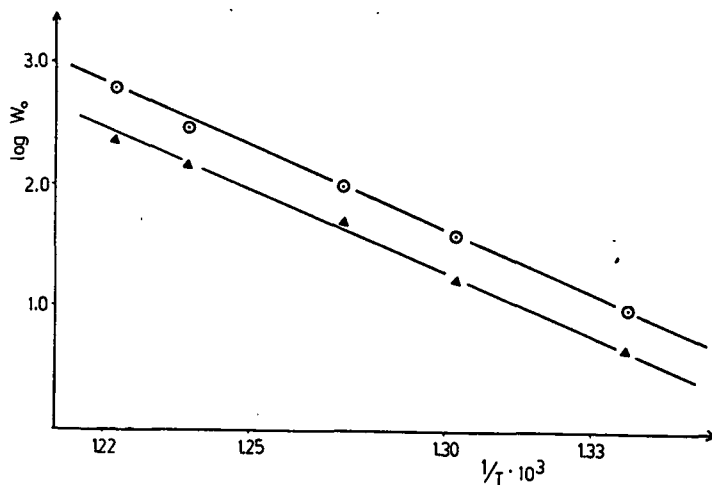


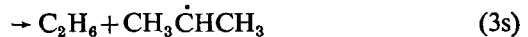
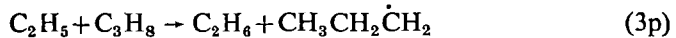
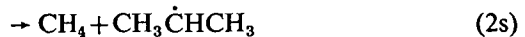
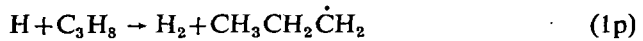
Fig. 8. $\log w_0$ vs. $1/T$ plots for hydrogen (Δ) and methane (\circ)

Discussion

In a preceding paper [2] a mechanism was set down which was able to describe the decomposition of propane to a good approximation in a recirculation system. When an olefin-absorber is used, the mechanism of the decomposition will be essentially simpler; with the continuous absorption of olefins formed during the decomposition, the reactions involving olefin participation are negligible. It is important to note that the absorption of olefins is practically complete at lower conversions and at temperatures below 535 °C.

From our experimental results when an olefin-absorber was used and from data to be found in the literature, the following simple mechanism can be given for the

thermal decomposition of propane



From this mechanism, the following expression can be given for the ratio $[\text{C}_4\text{H}]/[\text{H}_2]$:

$$\frac{[\text{CH}_4]}{[\text{H}_2]} = \frac{k_2}{k_1} \frac{[\text{CH}_3]}{[\text{H}]}$$

where

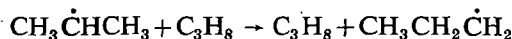
$$\frac{k_2}{k_1} = \frac{k_{2p} + k_{2s}}{k_1 + k_{1s}} \quad \text{and} \quad \frac{[\text{CH}_3]}{[\text{H}]} = \frac{k_1}{k_2} \frac{1}{\beta}$$

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

Hence

$$\alpha = \frac{[\text{CH}_4]}{[\text{H}_2]} = \frac{1}{\beta} \quad (\text{II})$$

This expression indicates that α is independent of the initial concentration of propane. This is in contradiction with our experimental results (see Fig. 6 and Table II). The difference probably originates from the insufficiency of the mechanism described. LEATHARD and PURNELL [3, 6] also observed the dependence of α on the propane concentration and conclude that this can be explained by the following bimolecular isomerization step



On the basis of our experimental results it is reasonable to suppose that the dependence of α on the propane concentration under self-inhibition-free conditions

is a consequence of the competition between the above bimolecular isomerization and the (sH) decomposition of *s*-propyl radicals. This assumption is supported by the observation that the extent of the concentration-dependence of α decreases with increasing temperature (see Fig. 4). With increasing temperature the decomposition reaction (sH), which has a higher activation energy, becomes of relatively greater importance, whereas the isomerization plays an ever smaller part and finally the competition of these two reactions gradually comes to an end.

Table IV

Experimental and calculated α values at propane pressure
 $p=61$ Torr (in the presence of olefin-absorber)

°C	No.	conversion %	α experimental	α calculated (ZBM I)	α calculated (ZBM II)	α calculated (LP)
450	236	0.0498	0.705	1.440	—	—
	237	0.0869	0.642	1.440	—	—
	238	0.1530	0.560	1.440	—	—
	239	0.2061	0.615	1.440	—	—
475	208	0.211	0.633	1.466	—	0.619
	204	0.3185	0.648	1.466	—	0.620
	205	0.7550	0.611	1.466	—	0.623
	207	1.3320	0.631	1.466	—	0.624
	209	2.1010	0.678	1.466	—	0.637
495	174	0.5154	0.696	1.368	—	0.668
	172	1.1945	0.614	1.368	—	0.675
	176	1.2114	0.612	1.368	—	0.674
	173	2.3867	0.637	1.368	—	0.686
	175	4.1128	0.739	1.368	—	0.744
515	177	1.0997	0.563	1.623	1.623	0.682
	178	2.3538	0.665	1.623	1.623	0.689
	220	3.1989	0.701	1.623	1.622	0.694
	179	3.4133	0.658	1.623	1.623	0.699
	180	6.8679	0.660	1.623	1.624	0.725
535	189	3.40	0.715	1.643	1.664	0.704
	222	3.97	0.773	1.643	1.664	0.707
	190	6.093	0.683	1.643	1.669	0.732
	191	9.70	0.708	1.643	1.717	0.766
	217	9.50	0.714	1.643	1.645	0.795
	192	17.19	0.674	1.643	1.645	0.861
	193	25.25	0.732	1.643	1.646	0.952
	196	37.23	0.747	1.643	1.644	1.143
545	218	14.08	0.721	1.653	1.669	—
	216	14.25	0.653	1.653	1.680	—
	202	15.09	0.752	1.653	1.647	—
	203	29.20	0.777	1.653	1.673	—
	193	47.31	0.772	1.653	1.665	—
	200	56.01	0.673	1.653	1.645	—
	201	61.17	0.752	1.653	1.643	—

(ZBM I) calculated *via* expression (II), see text

(ZBM II) calculated *via* expression in Ref. [12]

(LP) calculated *via* expression (III), see Ref. [6]

Table V
Kinetic parameters used in the calculations

Reaction	log A (dm ³ mol ⁻¹ s ⁻¹)	E _a Kcal/mol	References
H + C ₃ H ₈ → H ₂ + P	11.1	9.7	[7]
→ H ₂ + S	10.8	7.7	[7]
CH ₃ + C ₃ H ₈ → CH ₄ + P	9	11.5	[8]
→ CH ₄ + S	8.8	10.5	[7]
P → H + C ₃ H ₈	13.2	38.6	[7]
→ CH ₃ + C ₂ H ₄	13.1	32.5	[7]
S → H + C ₃ H ₈	13.9	40.4	[7]
→ CH ₃ + C ₂ H ₄	14.6	44	[9]
H + C ₃ H ₆ → P	9.9	2.9	[10]

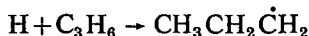
By means of expression (II), α values were calculated from the result, obtained in the presence of absorber; these data are collected in column 5 of Table IV. The experimentally determined α values can be found in column 4. The Arrhenius parameters used in these calculations are shown in Table V. Table IV reveals that α values calculated *via* expression (II) differ from the experimental α values by a factor of 2, similarly as in the absorber-free experiments (see [2]). This difference between the two sets of data may originate from the inaccuracy of the Arrhenius parameters used in the calculations.

If a more complicated expression (involving the concentrations of propane and olefins) is used for the calculation of α (see [2]), the α values in column 6 of Table IV are obtained. These values are in good agreement with the values calculated with expression (II).

According to LEATHARD and PURNELL [6], at low conversions (<2%) the following simple expression can be given for the ratio of methane to hydrogen

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

where k_{p-H} is the rate constant for the reaction



The α values calculated using expression (III) are given in column 7 of Table IV. As can be seen from the data and from Figs. 9 and 10, in the temperature range 475–515 °C, at low conversions (<5%), similarly as in the absorber-free experiments there is a good agreement between the experimental and calculated α values. At 535 and 545 °C and at higher conversions (>5%), a significant positive error appears, and in addition the calculated α values increase significantly with the conversion (Fig. 10).

The results discussed above indicate that with the use of an olefin-absorber the self-inhibition taking place during the thermal decomposition of propane can easily be decreased or stopped completely, and consequently the kinetics of decomposition

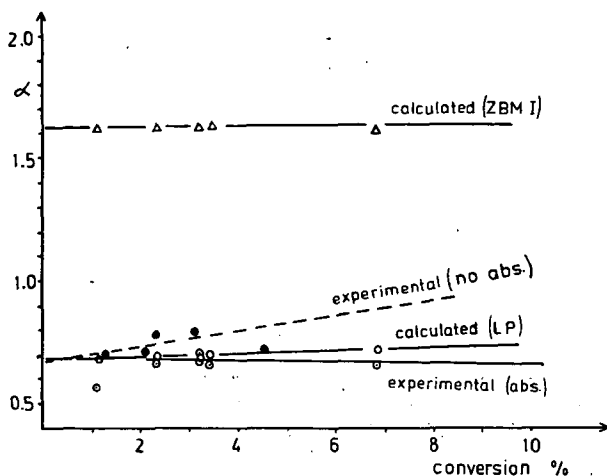


Fig. 9. Dependence of α on conversion (propane pressure, $p_0=61$ Torr, $t=515$ °C). experimental (abs.): experimental points (using olefin-absorber), calculated (LP): points calculated *via* the expression of Leathard and Purnell, experimental (no abs.): experimental points (without olefin-absorber), calculated (ZBMI): points calculated *via* the expression of Zalotai, Bérces and Márta

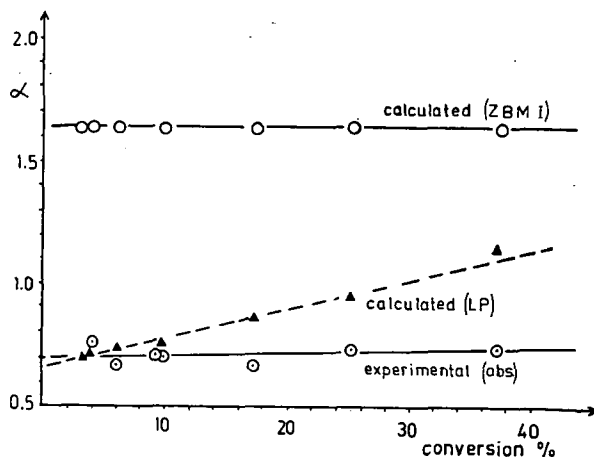


Fig. 10. Dependence of α on conversion (propane pressure, $p_0=61$ Torr, $t=535$ °C). experimental (abs.): experimental points (using olefin-absorber), calculated (LP): points calculated *via* the expression of Leathard and Purnell, calculated (ZBMI): points calculated *via* the expression of Zalotai, Bérces and Márta

will be significantly simpler. The mechanism described for the kinetics of decomposition is in accord with the experimental results. It is necessary, however, to complement this mechanism, with the bimolecular isomerization step proposed first, by LEATHARD and PURNELL.

Acknowledgements

The authors are grateful to Mrs. M. Tóth and T. P. Árnayas for technical assistance.

References

- [1] Bárdi, I., T. Bérces: *Acta Phys. et Chem. (Szeged)* **28**, 153 (1962).
- [2] Bárdi, I., T. Bérces: *Acta Phys. et Chem. (Szeged)* **28**, 161 (1982).
- [3] Leathard, D. A., J. H. Purnell: *Proc. Roy. Soc.* **A306**, 553 (1968).
- [4] Laidler, K. J., N. H. Sagert, B. W. Wojciechowski: *Proc. Roy. Soc.* **A270**, 242 (1962).
- [5] Zalotai, L., T. Bérces, F. Márta: *Magyar Kém. Folyóirat* **78**, 335 (1972).
- [6] Leathard, D. A., J. H. Purnell: *Proc. Roy. Soc.* **A305**, 517 (1968).
- [7] Allara, D. L., R. Shaw: *J. Phys. Chem. Ref. Data* **9**, 523 (1980).
- [8] Jackson, W. M., J. M. McNesby, B. de B. Darwent: *J. Chem. Phys.* **37**, 1610 (1962).
- [9] Szivovics, L., I. Szilágyi: *Int. J. Chem. Kinetics* **12**, 113 (1980).
- [10] Kerr, J. A., M. J. Parsonage: *Evaluated Kinetic Data on Gas Phase Addition Reactions*, Butterworth, 1972.
- [11] Zalotai, L., F. Márta, T. Bérces, D. Halász: *Ox. Communications* **1**, 85 (1979).
- [12] Zalotai, L., T. Bérces, F. Márta: *Magy Kém. Folyóirat* **78**, 549 (1972).

ТЕРМИЧЕСКИЙ РАСПАД ПРОПАНА В РЕЦИРКУЛЯЦИОННОЙ СИСТЕМЕ III. ИССЛЕДОВАНИЕ В ПРИСУТСТВИИ АДсорбЕНТА ОЛЕФИНОВ

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Проведен пиролиз пропана в рециркуляционной системе в присутствии адсорбента олефинов при температурах в области 450—545 °С, давлении пропана 30—470 Торр, в широком диапазоне конверсии (0,1—72%). В принятых экспериментальных условиях отношение метана к водороду (α) не изменяется с изменением конверсии, α несколько меняется с температурой. Зависимость α от концентрации пропана является функцией температуры. Предложен простой механизм реакции на основании литературных данных и полученных экспериментальных результатов. Значение величин α , рассчитанных на основании предложенного механизма, находятся в хорошем согласии с экспериментально найденными значениями.