

**THERMAL DECOMPOSITION OF PROPANE IN A
RECIRCULATION SYSTEM, I.
A SIMPLE APPARATUS FOR THE PRODUCTION OF
SELF-INHIBITION-FREE EXPERIMENTAL CONDITIONS**

By

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A simple, all-glass circulation system was constructed in which the self-inhibition occurring in the pyrolysis of short-chain paraffins can be eliminated using an olefin-absorbent.

The rates of many decomposition reactions in the gas phase decrease with time much more markedly than can be explained on the basis of the consumption of the starting material. This phenomenon is called self-inhibition, it is frequently observed in the thermal decomposition of paraffin hydrocarbons. Except for *n*-butane, the self-inhibition is detectable in the pyrolysis of all shorter-chain hydrocarbons, in the very early stages of the decomposition.

The phenomenon has been well known for 50 years, but intensive investigations started only in 1962. Since that time many papers have been published in this field. Mention should be made of the work of PURNELL ET AL. [1—5], NICLAUSE AND HIS COWORKERS [6—9], and ZALOTAI, BÉRCES, MÁRTA [10].

In most cases, the appearance of self-inhibition leads to a change in the product distribution too. On the basis of this experimental fact, LEATHARD [11] categorized this self-inhibition into three types:

- (i) No change in product distribution accompanies the self-inhibition.
- (ii) There is a small alteration in the product distribution as a sequence of the self-inhibition, only the products of chain termination changing:
- (iii) There is a significant change in the product distribution.

The self-inhibition is caused by the unsaturated products produced during the decomposition. On this basis two types of self-inhibition are mentioned in the literature. One type is "addition self-inhibition". In this case the reaction responsible for the self-inhibition is the addition of an atom (mostly H atom) or free radical to the double bond of a product olefin. The second type is "abstraction self-inhibition", in which the self-inhibition is produced by hydrogen abstraction from the olefin

molecules. It is believed that the structure of the decomposing olefin determines what type of self-inhibition occurs during the decomposition.

It can be seen from the foregoing that the formation of the product olefins has a very important effect on the decomposition of paraffin hydrocarbons. If in some way we can ensure the continuous removal of the olefins formed during the pyrolysis, we have an easy method in which the self-inhibition is eliminated. In this paper we describe a simple system in which we have tried to produce self-inhibition-free pyrolysis conditions. The decompositions were conducted in a recirculation system, and the product olefins were continuously absorbed by an olefin-absorber.

Experimental

The scheme of our apparatus is shown in Fig. 1. The apparatus consists of four main parts:

1. Part for producing and measuring the vacuum.
2. Part for storing the reagents.
3. Recirculation system, which consists of a stirred flow reactor, the circulation pump, and a U-tube containing the olefin-absorber.
4. Analysis part.

Before each experiment, the apparatus was carefully evacuated with a mercury diffusion pump to 10^{-4} Torr. The pressure was measured with a Penning-Pirani Vacuummeter (VEB Funk-Technik, DDR). The reagents were stored in 5 dm³ glass bulbs equipped with greaseless (Rotaflö) taps (Nos. 9 and 10 in Fig. 1). The reagents

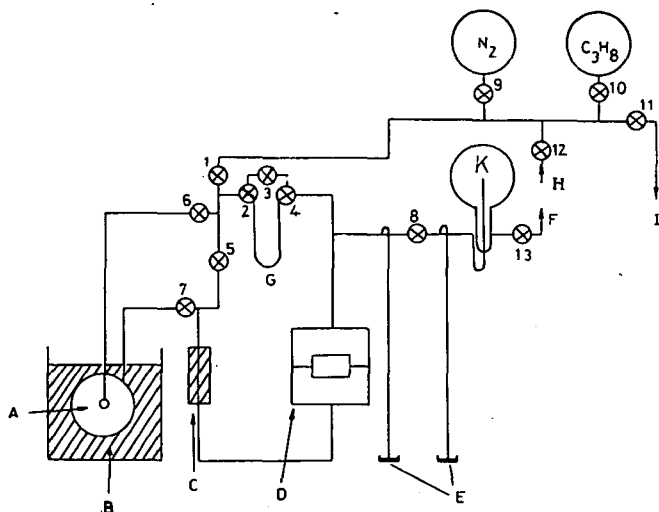


Fig. 1. Schematic diagram of the apparatus
 A stirred flow reaction vessel, B air-heated oven, C rotameter, D electromagnetic pump, E mercury manometers, F to the sampling valve, G olefin absorber, H reactant inlet, I to the vacuum, K bulb for collecting samples for g.c. analysis ⊗ denotes greaseless (Rotaflö) taps

were circulated by a horizontal electromagnetic pump. The piston of this pump was made of glass, and its inside was finely polished. The teflon-covered iron core was located in the piston. This iron core was moved by two oppositely conducting electromagnets (D_1 and D_2 in Fig. 2). The electromagnets were controlled by a transistorized multivibrator the amplitude and frequency of which were variable. To guarantee unidirectional gas flow, the two ends of the piston were supplied with glass check valves (B_1 — B_4 in Fig. 2). The circulation rate was varied between 3 and 65 dm³/hour in the pressure range 10—760 Torr. The working of the circulation pump was reliable; the output was constant with time. To adjust and to control the flow rate in the system, a rotameter built into the system was used (C in Fig. 1).

The decomposition was conducted in a stirred flow glass reactor, made after the description of MULCAHY [12] (see Fig. 3). The volume of the reactor was

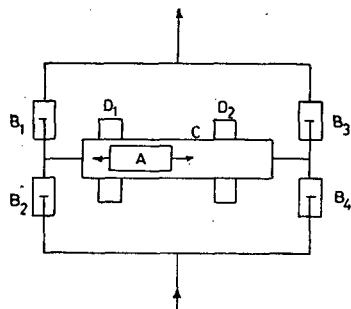


Fig. 2. Schematic diagram of the horizontal electromagnetic pump A teflon-coated iron core, B_1 — B_4 glass check valves, C piston house, D_1 , D_2 electromagnets

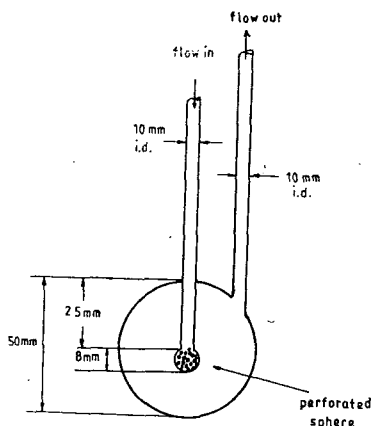


Fig. 3. Stirred flow reaction vessel

0.05291 dm³. It was positioned in an air-heated furnace (A and B in Fig 1); the temperature was measured with a Pt thermoelement. The temperature was constant to within $\pm 0.3^\circ\text{C}$.

Olefin-absorber. To attain the decrease of the self-inhibition, our first goal was to find a selective absorber which can immediately and with good efficiency absorb the olefins produced during the decomposition, but at the same time does not absorb the paraffin compounds.

Many methods are known in the literature for the absorption of gaseous olefins. One of the earliest methods was the use of sulfuric acid in the liquid form [3] or adsorbed onto a support [14] or the use of liquid sulfuric acid saturated with Ag_2SO_4 [14, 15]. The main disadvantages of these methods are that the absorber is very sensitive to water, it loses its capacity very quickly, and the absorption of ethylene and acetylene are not quantitative. Another very frequently used method is absorption using mercury (II) perchlorate (MP) [16—19]. In this method a gas-chromatographic

support is coated with MP. MP does not react with saturated hydrocarbons, whereas the unsaturated compounds remained in the form of complex compounds. Adding perchloric acid (PA) to MP significantly increases the capacity.

In our early investigations we tested different types of olefin absorbers. The best results were achieved with the MP—PA system, and in later studies we used this absorber. The MP—PA absorber was made by the reaction of HgO(red) with PA, the MP produced being coated onto a measured amount of g.c. support. (Type MHI, Reanal, Hungary). The concentration of this absorber solution was 1 mol/dm^3 (for MP and PA too). After the coating, the absorber was air-dried and until use it was stored in a dark, closed container. For experimental use the MP—PA absorber was taken in a glass U-tube which was connected to the circulation part of the apparatus (see G in Fig. 1). The U-tube was closed with greaseless taps 2 and 4. It was found to be easy to evacuate the absorber, which could be used for a long time without losing its capacity, and after the change of the absorber the experiments were reproducible. The absorber in the apparatus was stored under a nitrogen atmosphere in the dark. In our experiments the absorber was changed every 3 months.

Experimental methods used during pyrolysis of propane

Before any pyrolysis the system was carefully evacuated, the reaction vessel was filled with oxygen-free nitrogen to 1 atmosphere and taps 6 and 7 were closed (see Fig. 1). The U-tube containing the absorber was always evacuated only with a rotary oil pump (to avoid the complete dryness of the absorber, in which case its capacity decreases significantly); the U-tube was flushed out 3 times with pure nitrogen and was finally filled up to 1 atmosphere with nitrogen. The U-tube was closed by greaseless taps 2 and 4. The reactant at the desired pressure was admitted into the circulation system by opening taps 1, 3 and 5. After this, the circulation system was also filled up to 1 atmosphere with nitrogen.

To ensure good mixing of the paraffin-nitrogen mixture, before each experiment the gas mixture was circulated for 10 minutes with the electromagnetic pump. In runs in which the olefin-absorber was used, taps 2 and 4 were opened and tap 3 closed simultaneously and the circulation was continued for 10 minutes. The reaction was started by opening taps 6 and 7 and closing tap 5 simultaneously. During the experiments the reaction times were always longer than 15 minutes, to avoid mixing problems. The reaction was stopped by the opening of tap 8, and the contents of the reaction vessel and the circulation system were expanded into an evacuated bulb. (K in Fig. 1). The volume of this part of the apparatus was 0.56478 dm^3 (bulb + glass tubes together). The pressures of the samples were measured with the mercury manometer (E). From the sampling bulb, the samples were transferred into a gas sampling valve and their compositions were determined with g.c. methods. For evaluation of our experiments calibrations were performed using known concentrations of calibrant gases.

Results and Discussion

Determination of capacity of MP—PA absorber

It was very important for us to know the capacity of the absorber used in our experiments. The capacity measurements were made in the following way: pure olefin compounds (ethylene or propylene) were measured into the circulation system and the pressure was made up with oxygen-free pure nitrogen to 1 atmosphere. With taps 2 and 4 open (and simultaneously tap 3 closed) the olefin-nitrogen mixture was started to circulating through the absorber for a long time (4-6 hours). After this stage the olefin content of the mixture was determined with g.c. methods. The partial concentrations of olefins examined were chosen to be very close to the maximum concentration of olefins produced during the pyrolysis (in our case about 10 Torr). From the results it emerged that at maximum olefin concentrations (~ 10 Torr) complete absorption did not take place (even with a 6-hour circulation), but a small concentration of ethylene and propylene remained. The pressure of the remaining olefin was about $2 \cdot 10^{-2}$ Torr. This olefin level did not change when the experiment was repeated with fresh absorber. (The detection limit of olefins in our system was $5 \cdot 10^{-3}$ Torr.).

Determination of residence time distribution

It is very important to know the residence time distribution of the reactor because from this conclusions can be drawn on the flow conditions and the effectiveness of the mixing in the system. The fluid elements flowing through the reactor, even an ideal case, do not spend the same time in the reactor (*i.e.* the residence time changes). We measured the residence time distribution with a tracer method [20]. The essence of this is as follows: At time = 0, we instantaneously inject a known amount of tracer into the flow of fluid, and measure the concentration of the tracer in the exit stream as a function of time. Let $c(t)$ represent the concentration of tracer in the effluent at time t , and let v be the flow rate of fluid through the vessel. Between times t and $t + dt$ the amount of tracer in the exit stream is

$$q_0 E(t) dt = c(t) v dt$$

where q_0 is the amount of tracer injected into the stream, and $E(t)$ is the residence time density function [21, 22]. By definition $E(t) dt$ denotes the fraction of tracer leaving the system between times t and $t + dt$. From this

$$E(t) = v/q_0 c(t)$$

Hence by suitable transformation, the $c(t)$ curve is converted to $E(t)$. Introducing θ , the relative residence time, where

$$\theta = t/\bar{t}$$

(t = real residence time and \bar{t} = apparent residence time)

$$E(\theta) = \bar{t} e^{-\theta} \quad \text{or} \quad \log E(\theta) = \log \bar{t} - \theta$$

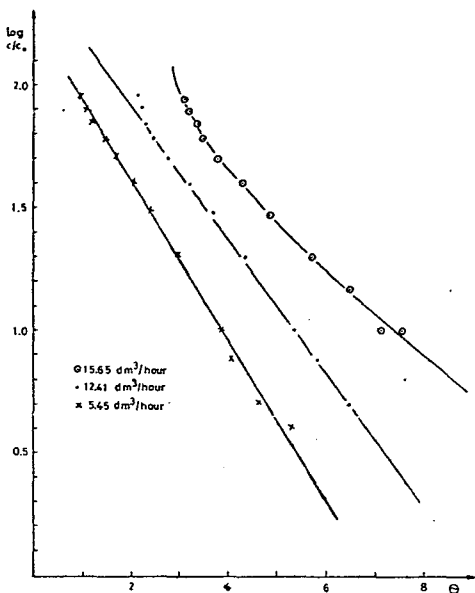


Fig. 4. Plots of $\log c/c_0$ vs. θ at different flow rates (N. B. curve B is transferred by 1 and curve C by 2 units on the θ axis, for convenience)

If the reactor is an ideal, well-mixed reactor, $\log E(\theta)$ vs. θ plots give straight lines.

The residence time distribution of our reactor was determined in the following way: the reactor was positioned in the thermostatic chamber of the g.c. apparatus (Carlo Erba ATC/f, equipped with TC detector) and connected into the g.c. line. As tracer, propane was used; this was injected *via* gas sampling valve, the amount of sample being 0.5 ml. Nitrogen was used as carrier gas. After the injection of the tracer into the reactor, the recorder of the chromatograph directly gave the $c(t)$ curve. The tracer measurements were made at 150 °C, a detector current of 170 mA and a chart speed of 1/3—1/4 inches per min. The flow rate of carrier gas being varied in the range 5.5—16.5 dm³/hour. Log c/c_0 values (which were calculated from the $c(t)$ curves)¹ were plotted against θ (where $\theta = tv/V$, V is the volume of the reactor and v is the flow rate in dm³/hour).

Some typical experimental results are shown in Fig. 4. It can be seen that at a flow rate of 12 dm³/hour the $\log c/c_0$ vs. θ plot gives a good straight line, *i.e.* our reactor behaves as a well-stirred reactor. Above and below this flow rate there are minor deviations from the linearity.

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ТЕРМИЧЕСКИЙ РАСПАД ПРОПАНА В РЕЦИРКУЛЯЦИОННОЙ СИСТЕМЕ I.
ПРОСТОЙ ПРИБОР ДЛЯ СОЗДАНИЯ ЭКСПЕРИМЕНТАЛЬНЫХ УСЛОВИЙ
С ИСКЛЮЧЕНИЕМ САМОИНГИБИЦИИ

И. Барди, Т. Берцеш

Описано создание экспериментальных условий с применением олефинабсорбера для исключения самоингибции при пиролизе углеводородов с низким молекулярным весом.