382. *The Kinetics of the Thermal Decomposition of Olefins. Part I. Propylene.*

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The thermal decomposition of propylene in a static system has been investigated over a pressure range of 50—500 mm. and a temperature range 570—650°. Analyses of the products of the reaction were made at various stages, temperatures, and pressures. The observed pressure increase was shown to be a measure of the propylene decomposed for the first half of the reaction.

The decomposition was a homogeneous first-order reaction with activation energy 57·1 kcals./g.-mol.

The products of decomposition are mainly methane, ethylene, hydrogen, a condensable intermediate which subsequently decomposes, and carbon. A mechanism of decomposition has been suggested.

Below 570° polymerisation occurs as well as decomposition.

The thermal decomposition of a normal saturated paraffin yields an olefin and a lower paraffin. In making a detailed study of this decomposition it is therefore important to know the relative stability of the olefinic portion of the product. In the pyrolysis of the higher paraffins (*e.g.*, *n*-heptane), secondary decomposition of the products gives rise to a sigmoid type of Δp–time curve; if all the products and their rates of decomposition are known, it should be possible to analyse this sigmoid curve (Stubbs and Hinshelwood, *Proc. Roy. Soc.*, 1950, *A*, **200**, 458 *et seq.*). When the products from the decomposition of these higher paraffins are examined, it is important to know whether the ethylene and propylene have been produced in the primary rupture of the paraffins, or by a secondary reaction of a larger olefin.

For a study of the olefin series, propylene seemed a convenient starting point, and although several investigations have been made in recent years none of them applied to the conditions in which the paraffin decomposition has been studied in this laboratory (Frey and Smith, *Ind. Eng. Chem.*, 1928, **20**, 948; Burnham and Pease, *J. Amer. Chem. Soc.*, 1942, **64**, 1404; Szwarc, *J. Chem. Physics*, 1949, **17**, 284; Hurd and Meinert, *J. Amer. Chem. Soc.*, 1930, **52**, 4978).

Experimental.

The apparatus and experimental technique have already been described (Stubbs and Hinshelwood, *Proc. Roy. Soc.*, 1950, *A*, **200**, 458). Propylene was prepared from pure *iso*propyl alcohol by the action of phosphoric oxide. Alcohol carried over with the propylene was removed in a trap cooled to 0°. The propylene was then condensed in a liquid-air trap and fractionated, a small middle fraction only being collected.

The gaseous products of the reaction were analysed by the conventional methods with a Bone and Wheeler apparatus: the principal products were hydrogen, methane, and ethylene. Unchanged propylene was measured by absorption in 82·4% sulphuric acid (Hurd and Spence, *J. Amer. Chem. Soc.*, 1929, **51**, 3353). Ethylene was absorbed with saturated mercuric acetate. Hydrogen was determined by slow combustion at 275° over copper oxide, and methane by explosion with oxygen.

Carbon dioxide was used as a reference gas, a known amount (about one-sixth of the propylene pressure) being added to the propylene. Analysis of the ratio of carbon dioxide to propylene after pyrolysis showed how much propylene had decomposed. Preliminary experiments showed that the addition of carbon dioxide had no effect on the course of reaction.

General Form of the Δp–*Time Curves.*—The change of pressure during the decomposition of 300 mm. of propylene at four different temperatures is shown in Fig. 1. At low temperatures the initial part of the reaction is a polymerisation and there is at first a decrease of pressure, followed after some time by an increase. At higher temperatures there is little or no negative pressure change at the beginning, though the initial rate is still zero or very small (even at 630°). The rates taken from the Δp–time curves for comparative purposes were therefore maximum rates (not initial rates as previously with the paraffins), the initial rates being useless as criteria for comparison.

In order to find out how far these Δp–time curves are a definite measure of the rate at which propylene is consumed, the amounts of residual propylene and of reaction products were determined by analysis over the course of the reaction. The curve for propylene consumed proves in fact to be of the same general form as the Δp–time plots (Fig. 2). If the comparison of the Δp–time plots at different temperatures and pressures is to have any real meaning it is necessary to find out whether for a given pressure the same Δp corresponds at all temperatures to the same amount of propylene decomposed, and similarly whether at a given temperature the same Δp : initial pressure ratio corresponds to the same percentage decomposition of the propylene.

FIG. 1.

Δp–*Time curves for the decomposition of* 300 *mm. of propylene at various temperatures.*

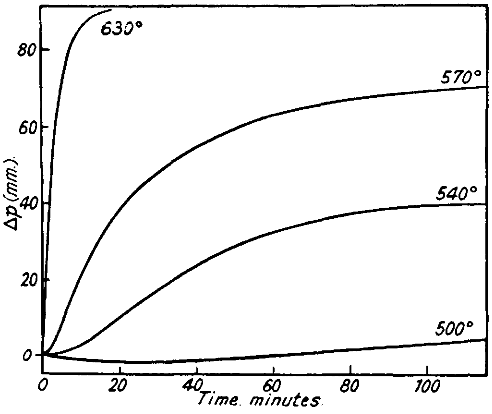
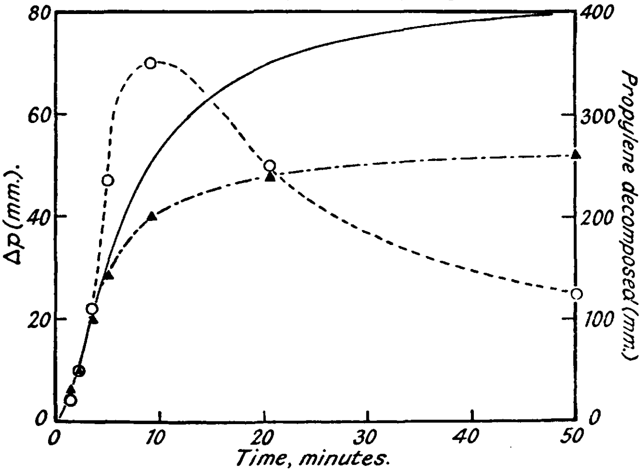


FIG. 2.

Thermal decomposition of 300 *mm. of propylene at* 600°.



Unbroken curve—observed pressure change ; ▲—*propylene consumed* (*right-hand scale*) ; ○—*condensable product* (*left-hand scale*).

In Fig. 3 the observed Δp for the decomposition of 300 mm. of propylene for the temperature range 500—630° is plotted against the propylene consumed. It is seen that from 570° to 630° during the initial third of the reaction the curves are coincident. Below 570°, however, for a given Δp more propylene is used up. Fig. 4, moreover, shows that it is permissible to compare Δp–time curves for different initial pressures, at constant temperature. The " induction period " of a Δp–time curve is taken as the time from the start of the reaction to the point on the axis cut by a tangent at the point of maximum slope of the curve. It decreases with rise of temperature and varies from 1½ minutes to a few seconds over the temperature and pressure range covered in the study of the activation energy.

Variation of Rate with Pressure.—The variation of rate, r, with initial propylene pressure is recorded for a series of temperatures in Fig. 5. At each temperature the reaction is of first order with a characteristic transition to second-order kinetics at lower pressures (a plot of p_0/r against $1/p_0$ gives a straight line). Other workers on the decomposition of propylene have stated that the reaction is of the first order.

A plot of log (maximum rate) against the reciprocal of the absolute temperature for an initial propylene pressure of 300 mm. is a straight line from 630° to 520°. (At 500° the rate falls below this line.) The activation energy calculated from this plot was 57·1 kcals./g.-mol. In order to make this investigation comparable with the recent work on the variation of activation energy with pressure for the fully inhibited decompositions of normal paraffins (Ingold, Stubbs, and Hinshelwood, *Proc. Roy. Soc.*, 1950, *A*, **203**, 486), the activation energy of the propylene decomposition was studied from 50 to 500 mm. pressure over a temperature range from 590° to 650°. Little or no variation was found.

FIG. 3.

Thermal decomposition of 300 mm. of propylene at various temperatures: plot of observed Δp *against propylene decomposed.*

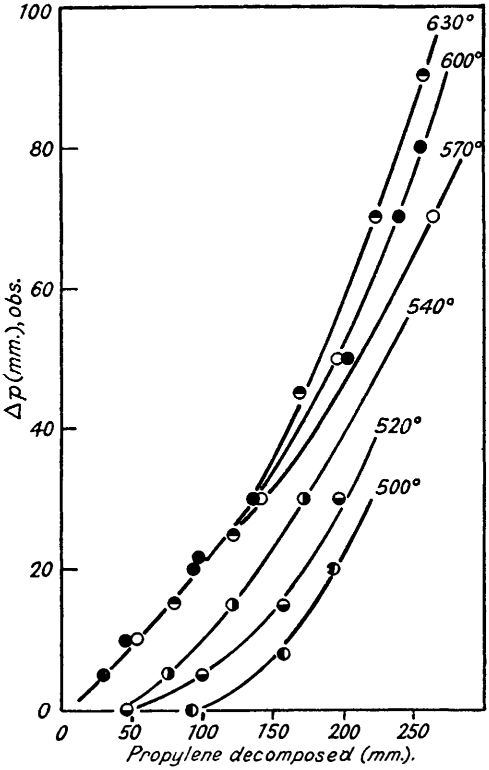
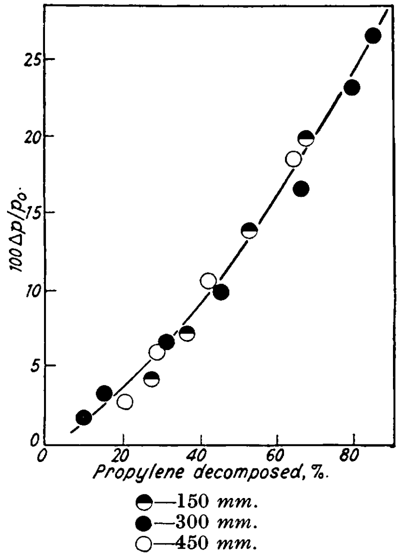


FIG. 4.

Thermal decomposition of propylene at 600°: plot of percentage pressure change against percentage of propylene decomposed.



Since from 630° to 570° curves of Δp against propylene decomposed are coincident in their initial regions, the Δp–time curves for a given pressure can be compared in terms of the times required for a definite increase of pressure. A plot of log (time for Δp = 30 mm.) against $1/T$ for an initial pressure of 300 mm. in fact yields a straight line from 630° to 520°. The activation energy calculated from it is 56·7 kcals./g.-mol., in agreement with that obtained from the maximum rates.

Experiments with a packed reaction vessel showed that the rate of decomposition of propylene was reduced slightly. Measurements at different temperatures, however, proved the activation energy to be the same as in the unpacked vessel.

Investigation of Reaction Products.—Except for the work of Burnham and Pease on the polymerisation of propylene at 500°, its thermal decomposition has always previously been studied in a flow system. All workers found methane and ethylene to be the main reaction products, together with smaller amounts of hydrogen, ethane, and higher hydrocarbons. In all cases the ratio of methane to ethylene was found to be roughly 1 : 1. The present analytical work shows, however, that the relative concentrations of the products in a static system are entirely dependent on the degree of decomposition (Fig. 6), the product molecules being subject to further reaction. Even at a rather low percentage conversion (8%) the ratio of methane to ethylene (at 600°) is nearer 2 : 1 (Fig. 6). This ratio remains about the same up to about 70% decomposition. It then becomes even larger, because the concentration of ethylene passes through a maximum (after about 80% reaction). The concentration of methane on the other hand continues to increase throughout the course of the reaction. The hydrogen concentration follows that of ethylene. Similar results were obtained by Hurd and Meinert (*loc. cit.*), who found that the concentration of methane increases with increasing temperature and time of contact.

In their analytical work Hurd and Meinert were able to account for most of the hydrogen as molecular hydrogen, gaseous hydrocarbons, or liquid polymers, but they were not able to account for all the carbon.

FIG. 5.

Rate–pressure curves for propylene decomposition at various temperatures.

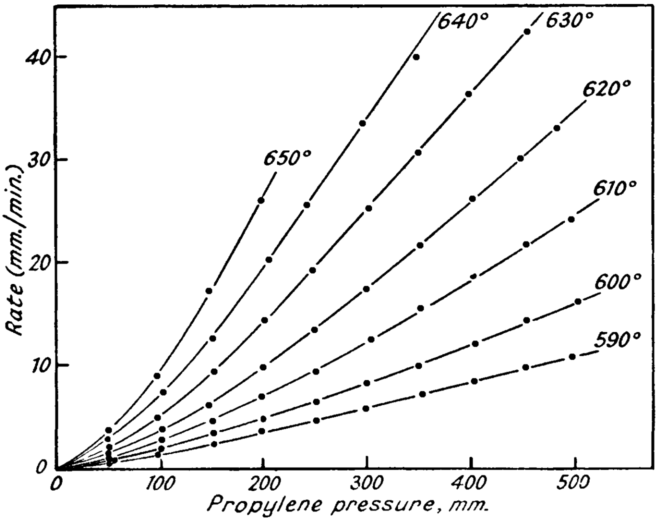


FIG. 6.

Thermal decomposition of 300 *mm. of propylene at* 600° *: variation of reaction products with time.*

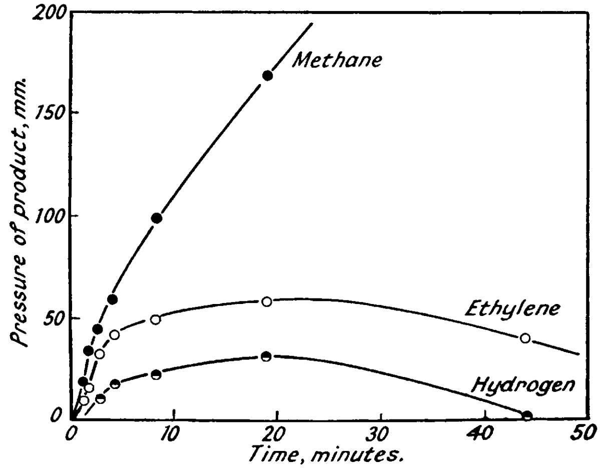


Fig. 7 shows the percentage of hydrogen and carbon accounted for in the present work in the gaseous products during the decomposition of 300 mm. of propylene at 600°. Similar curves were obtained at all the temperatures at which analyses were made. Nearly all the hydrogen is accounted for at the beginning and end of the reaction. Only two-thirds of the carbon is ever accounted for, and during most of the reaction a large proportion of both carbon and hydrogen fail to appear in the gas analysis. This fact must be explained by a polymerisation of propylene to liquid polymers and tars which condense and escape analysis. Elementary carbon is deposited on the walls of the reaction vessel in shiny hard flakes. Between 680° and 870° Szwarc found no involatile or polymeric substances, but the conversions were low. Hurd and Meinert at 600—700° found carbon deposition together with the formation of aromatic liquids and a small amount of a heavy tar. They found that 20—25% of the propylene used was converted into aromatic liquids.

In the present investigation the concentration of condensable products (liquid polymers) was determined in two ways : (1) Subtraction from the total pressure at the time of sampling gives the pressure of condensable products; (2) the gaseous products in the reaction vessel were shared with an evacuated vessel cooled in solid carbon dioxide and acetone. The sharing factor between the two vessels was measured with propylene (which did not condense). The liquid polymers condensed out in spite of their low partial pressure. From the final pressure the amount of condensable material in the reaction vessel could be calculated. Results obtained by the two methods were in good agreement.

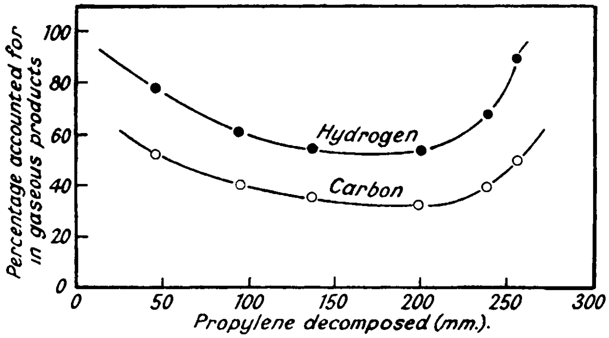
Fig. 2 shows how the condensable products increase steadily to a maximum and then gradually decrease towards the end of the reaction. The maximum occurs when about two-thirds of the propylene has been consumed, and as indicated in Fig. 2, the pressure of condensable products is slightly greater than the observed Δp at this point.

Hurd and Meinert identified benzene and toluene in the liquid polymer, and found indications of naphthalene and phenanthrene. They found no allene or polymers of allene among the products. At a considerably higher temperature, however, Szwarc found allene and a small quantity of diallyl.

For a rough identification of some of the substances formed a cooling curve of the gaseous products was determined (after a rapid cooling to 400° to freeze the reaction). Steps in the curve gave indications of a C_6 or C_7, a C_{10}, and a C_{12} compound. Moor, Strigaleva, and Frost (*J. Gen. Chem. U.S.S.R.*, 1937, **7**, 860) pyrolysed and polymerised propylene at atmospheric pressure from 610° to 720° by a flow method. They found the products to be about half liquids composed of hydrocarbons with 5, 6, 7, and more carbon atoms, chiefly olefins and aromatic compounds. The gaseous products were methane, ethylene, and hydrogen.

FIG. 7.

Thermal decomposition of 300 *mm. of propylene at* 600° : *percentage of carbon and hydrogen accounted for in gaseous products.*



Effect of Nitric Oxide.—Propylene, like nitric oxide, acts as an inhibitor of chains in the decomposition of the normal paraffin hydrocarbons, and it is therefore interesting to find whether it is itself able to inhibit completely any chains that may start in it. Experiment shows that the addition of nitric oxide in any but the smallest amounts produces an increase of rate. Less than 2% of nitric oxide appears to reduce the rate very slightly. Analysis shows that when the rate is increased by nitric oxide, the latter is consumed as the reaction proceeds. Carbon monoxide and carbon dioxide are also found in the reaction products, so that some oxidation reaction occurs. The absence of appreciable inhibitory effects at low concentrations of nitric oxide suggests strongly that chain reactions are not playing an important part in the total reaction.

DISCUSSION.

From the foregoing evidence we conclude that at temperatures around 500° propylene polymerises with consequent decrease of pressure. The polymerisation is assumed to be bimolecular, and the dimer first formed can react with more propylene to give higher polymers which can then react to give tars and gaseous products.

Fig. 3 shows how polymerisation and decomposition compete. At higher temperatures the decomposition predominates, and from 570° to 630° the observed Δp measures the propylene consumed as long as Δp does not exceed 30 mm. at an initial pressure of 300 mm., *i.e.*, about half the propylene decomposed. As shown in Fig. 7, the deficiency of hydrogen and carbon in the gaseous products increases rapidly at the beginning of reaction. At first, all the hydrogen is probably accounted for, and possibly all the carbon. Only near the end does the balance of hydrogen rise towards 100%, but that of carbon does not. The inference from this is that the decomposition occurs with the formation of both gaseous and condensable products. Some of the latter are stable nearly to the end, and they then gradually yield gases and deposit solid carbon. It is noteworthy that a proportion of the condensable products is fairly stable until two-thirds of the propylene has been consumed.

The Δp–time curves in Fig. 1 show an upward curvature before attaining the maximum rate. This " lag " gets less as the temperature rises. These facts suggest that the propylene at first decomposes without change of pressure to give intermediates which subsequently decompose further, these subsequent decompositions setting in sooner at higher temperatures.

As shown in Fig. 5, the reaction is of the first order (except at low pressures when the characteristic transition to second-order kinetics occurs). The use of these results is justified by those given in Fig. 4, where the percentage pressure change is shown to be a measure of the percentage propylene consumed for three different initial pressures. Therefore we suggest that the initial reactions may be represented by :

$$\text{propylene} \longrightarrow \text{A} + \text{B} \qquad \text{(slow)} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

$$\text{A} + \text{propylene} \longrightarrow \text{C} \qquad \text{(fast)} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

(i) and (ii) jointly give rise to no change of pressure. The product C must obviously suffer a series of reactions, accompanied by an increase of pressure.

Fig. 2 shows that the condensable products increase steadily until two-thirds of the propylene has been consumed (cf. hydrogen and carbon deficiency in Fig. 7). Methane and ethylene increase steadily up to $\Delta p > 30$, *i.e.*, when more than half the propylene has decomposed. Also the observed rate rises quite rapidly to a maximum, though not immediately (Fig. 1). Therefore we must suppose that we have

$$\text{C} \longrightarrow \text{D} + \text{E} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii)}$$

followed possibly by

$$\text{propylene} + \text{D} \longrightarrow \text{D}' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iv)}$$

$$\text{D}' \longrightarrow \text{D}'' + \text{E}' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v)}$$

E and E′ are gases of low molecular weight, but eventually D″ is a polymer which is free enough from hydrogen to be relatively stable nearly to the end of the reaction. In the slow last stages it decomposes to give more gas and deposits carbon.

Fig. 6 shows that in the very early stages of the reaction methane is formed more freely than ethylene, and this suggests that B is in fact CH_4 and equation (i) becomes

$$C_3H_6 \longrightarrow CH_4 + C_2H_2{}^{*} \qquad (^{*} = \text{activated})$$

The product C in equation (ii) would therefore be $CH_3{\cdot}CH_2{\cdot}CH{:}C{:}CH_2$ or $CH_3{\cdot}CH{:}CH{\cdot}CH{:}CH_2$. This on decomposing could yield $CH_3{\cdot}C{\vdots}CH + C_2H_4$ [*i.e.*, D + E in (iii)]. Up to this stage the ethylene formed is equal to the methane, so we may suppose that the process continues

$$\underset{\text{(D)}}{CH_3{\cdot}C{\vdots}CH} + \text{propylene} \longrightarrow \underset{\text{(D}'\text{)}}{CH_3{\cdot}CH_2{\cdot}CH{:}C{:}CH{\cdot}CH_3} \quad . \quad . \quad \text{(cf. iii)}$$

$$\longrightarrow \underset{\text{(D}''\text{)}}{CH_2{:}C{:}C{:}CH{\cdot}CH_3} + \underset{\text{(E}'\text{)}}{CH_4} \quad . \quad . \quad \text{(cf. iv)}$$

The compound $CH_2{:}C{:}C{:}CH{\cdot}CH_3$ and compounds of similar type decompose slowly, and its concentration builds up nearly until the end of reaction. The above reaction scheme without any addition would mean that

$$3\ \text{propylene} \longrightarrow 2CH_4 + C_2H_4 + \text{D}''$$

i.e., that the amount of methane should be twice that of ethylene, and as shown in Fig. 6, for the first two-thirds of reaction this is true. Also ethylene should equal Δp, and reference to Figs. 2 and 6 confirms this. Again, the value of Δp should equal the formation of D″ and Fig. 2 shows that up to $\Delta p = 30$ this is so. The condensable products (D″) accumulate steadily until over half the propylene has reacted. The maximum concentration of condensable products is rather more than the observed Δp, but in a static system many condensation reactions can occur.

Another interesting feature is that if the carbon defect, expressed as the number of carbon atoms, is divided by the concentration of condensable product, the result indicates about 6 atoms of carbon to each molecule of condensable polymer.

Chains cannot be propagated in propylene over the temperature range used in this investigation, since it is an inhibitor. At higher temperatures, where the allyl radical ($C_3H_5\cdot$) may not be particularly stable, it is quite possible that a radical mechanism, with or without the propagation of chains, may predominate. This mechanism would have a higher activation energy, as found by Szwarc, whose measurements were made over a temperature range some 200° higher than the present ones.

It may be concluded then that over the range 570—650° propylene decomposes mainly by a molecular rearrangement reaction, the suggested mechanism accounting for the available experimental results. Since the reaction has first-order kinetics, steps (ii) and (iv) must be very much faster than the others. Step (iii) is rather faster than step (i) (unimolecular and rate-determining), and the concentration of C soon reaches a small steady value. The condensable product D″ is virtually an end product as far as concerns the part of the reaction where the kinetics are studied.

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