

563. *The Thermal Decomposition of n-Pentane.*

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The thermal decomposition of *n*-pentane has been further investigated. The results are interpreted on the assumption that the normal decomposition consists of (1) a molecular rearrangement process, and (2) a chain reaction repressible by nitric oxide.

Analysis of the products of decomposition (in the presence of sufficient nitric oxide to suppress the chain reaction) indicates that the probability of an initial rupture at the C₍₂₋₃₎ linkage is about twice that of one at the C₍₁₋₂₎ linkage. When the molecule breaks at the C₍₂₋₃₎ linkage, ethane and propylene are more frequently formed than ethylene and propane.

The variation with initial hydrocarbon pressure (p_0) of the rate (r_0) of the uninhibited reaction and r_∞ that of the fully inhibited reaction is satisfied by an equation of the form

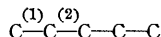
$$\text{rate} = a[p_0] + b[p_0]^2.$$

The apparent chain length (given by the ratio r_0/r_∞) decreases as p_0 increases.

The mechanism of the chain reaction seems to be generally similar to that of ethane.

MEASUREMENTS have been made of the rate of decomposition of *n*-pentane. The reaction was studied kinetically by measurement of pressure change in an apparatus which consisted essentially of an electrically heated furnace, silica reaction bulb, and a capillary manometer.

The products of decomposition (in the presence of sufficient nitric oxide to reduce the rate to its limiting value) were analysed by fractionation and chemical absorption. On the basis of the assumption that under these conditions all chain reaction is suppressed and that decomposition takes place by a molecular rearrangement, the chances that the pentane molecule breaks in positions (1) and (2) are calculated from the analytical results to be in the ratio 1 : 2. When the molecule breaks in position (2) the products ethane + propylene are formed in greater amounts than the alternative products ethylene + propane.



A study has been made of the influence of pressure and nitric oxide on the reaction rate. The results are interpreted in terms of the assumption that the reaction consists of two parts, viz.:

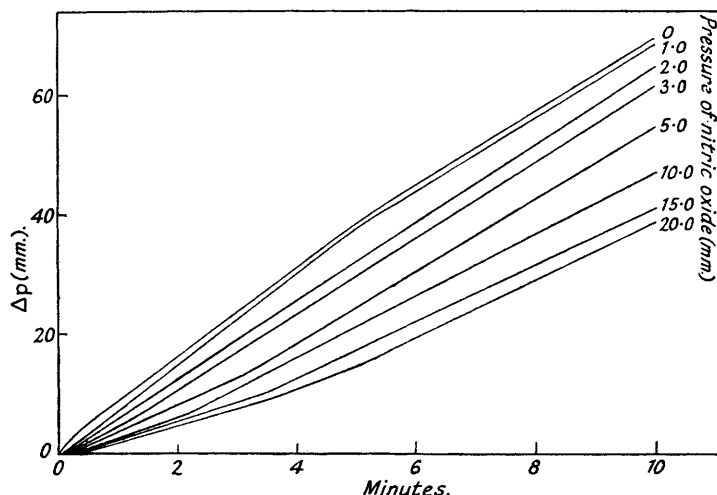
(1) A molecular rearrangement process for which the energy of activation is about 76 kcal./g.-mol.

(2) A chain reaction repressible by nitric oxide.

EXPERIMENTAL METHODS.

The apparatus and experimental methods have already been described (Partington and Danby, *J.*, 1948, 2226).

FIG. 1.



Δp -Time curves for the thermal decomposition of 250 mm. of n-pentane at 530° in the presence of increasing amounts of nitric oxide.

In the reaction-velocity measurements the increase of pressure (Δp) was observed at various intervals of time, and the initial rate of decomposition obtained by drawing a tangent to the Δp -time curve.

All pressures were measured in terms of mm. of mercury, and all rates as mm./min.

REACTION VELOCITY MEASUREMENTS.

Normal Uninhibited Decomposition.—The exact assessment of the initial rate is a matter of some difficulty, since the plot of Δp against time shows a pronounced curvature near the origin, but afterwards approximates closely to a straight line. A typical Δp -time curve is shown in Fig. 1.

There appears to be a marked inhibition by the products during the initial stages of the reaction, and on this assumption the correct rate would be given by the slope of the tangent to the initial steep portion of the curve, measured at $t = 0$. Values obtained in this way are plotted to give the upper curve in Fig. 2. If the rates obtained from the straight portions of the Δp -time curves are plotted they give the lower curve in Fig. 2.

The more detailed investigation of the Δp -time curve near the origin (Fig. 1) having shown

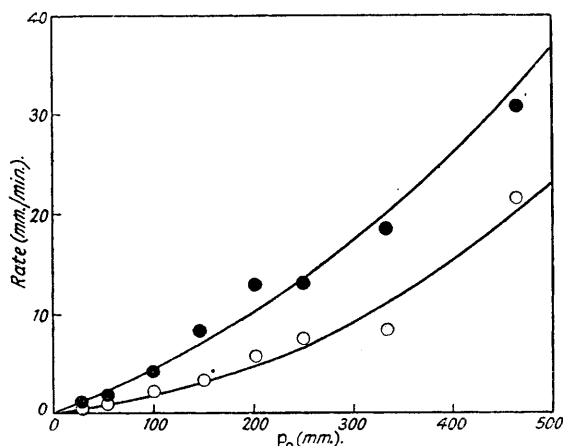
that the rapid change of curvature is real, it becomes obvious that the upper curve in Fig. 2 is in fact the correct one.

There is a similar pronounced curvature in the initial part of the Δp -time curve for the normal decomposition of *n*-butane (Steacie and Folkins, *Canadian J. Res.*, 1939, **B**, 17, 105; 1940, **B**, 18, 1).

The initial rate of decomposition of *n*-pentane at 530° c. was measured at various pressures up to 500 mm. The results are given in Table I. The upper curve in Fig. 2 shows how the initial rate r_0 varies with the initial hydrocarbon pressure p_0 . The curve is satisfied by the empirical equation

$$r_0 = 3.63 \times 10^{-2} p_0 + 7.33 \times 10^{-5} p_0^2.$$

FIG. 2.



Variation of rate with initial pressure for the uninhibited decomposition of *n*-pentane at 530°.

The lower curve in Fig. 2 is also satisfied by an equation of the same general form (with the first constant 0.92×10^{-2} and the second 7.37×10^{-5}).

Influence of Nitric Oxide.—Small amounts of nitric oxide cause a marked reduction of the decomposition rate. The effect of increasing amounts of nitric oxide on the Δp -time curve is shown in Fig. 1. It is seen that the effect of the first small additions is to flatten out the initial curved portion until it approximates closely to a straight line. The slope of the tangent to this line can easily be determined. The initial rates at 530° and 550° are reduced to a limit by the addition of increasing amounts of nitric oxide as shown in Tables II and III. In the latter are recorded the values of the function $(r - r_\infty)/(r_0 - r_\infty)$ where r = observed rate at a given p_{NO} , r_0 that when $p_{\text{NO}} = 0$ and r_∞ the limit reached at high values of p_{NO} .

TABLE I.

Normal uninhibited decomposition of *n*-pentane at 530°.

Initial pentane pressure p_0 (mm.)	29	54	100	146	202	250	333	465
Initial rate r_0 (mm./min.)	1.1	1.9	4.2	8.4	12.9	13.2	18.5	30.9

TABLE II.

Pressure of nitric oxide (mm.)	530°.		550°.	
	$p_0 = 100$ mm. Initial rate (mm./min.)	$p_0 = 250$ mm. Initial rate (mm./min.)	$p_0 = 100$ mm. Initial rate (mm./min.)	$p_0 = 250$ mm. Initial rate (mm./min.)
0	4.20	13.2	9.8	29.2
1.0	1.98	7.8	6.4	23.3
2.0	1.24	6.7	4.7	20.6
3.0	0.93	5.5	4.0	18.0
4.0	—	—	3.7	—
5.0	0.73	4.4	3.1	16.0
7.0	—	—	2.6	13.7
10.0	0.58	3.3	2.3	10.7
15.0	0.58	3.3	—	—
20.0	0.58	3.3	2.3	7.6

TABLE III.

Values of $(r - r_\infty)/(r_0 - r_\infty) = \{(\gamma[\text{NO}])^2 + 1\}^{\frac{1}{2}} - \gamma[\text{NO}]$.

Pressure of nitric oxide (mm.).	530°.		550°.	
	$p_0 = 100$ mm.	$p_0 = 250$ mm.	$p_0 = 100$ mm.	$p_0 = 250$ mm.
0	1.000	1.000	1.000	1.000
1.0	0.387	0.454	0.546	0.727
2.0	0.182	0.344	0.325	0.602
3.0	0.097	0.222	0.222	0.481
4.0	—	—	0.185	—
5.0	0.019	0.111	0.104	0.389
7.0	—	—	0.036	0.282
10.0	0	0	0	0.144
15.0	0	0	—	—
20.0	0	0	0	0
	$\gamma = 1.30$	$\gamma = 0.67$	$\gamma = 0.67$	$\gamma = 0.27$

According to the results of Hobbs and Hinshelwood (*Proc. Roy. Soc., 1938, A, 167, 439*) for the decomposition of ethane at 600°, the value of the function is given by

$$(r - r_\infty)/(r_0 - r_\infty) = \{(\gamma[\text{NO}])^2 + 1\}^{\frac{1}{2}} - \gamma[\text{NO}]$$

This expression fits the present results, with the values of γ given in Table III.

In the case of ethane, γ varied as $[\text{C}_2\text{H}_6]^z$ when z lay between -0.73 and -0.87 . With pentane the values of z are -0.71 at 530° and -0.99 at 550°.

The rate of the fully inhibited decomposition (r_∞) of *n*-pentane at 530° was measured at a series of initial hydrocarbon pressures. The results are given in Table IV. The dependence

TABLE IV.

Fully inhibited decomposition of *n*-pentane at 530°.

Initial pentane pressure, p_0 (mm.) ...	46	98	100	144	147	199	250	301	350	404	421	460
Initial rate, r_∞ (mm./min.)	0.23	0.55	0.58	1.03	1.14	2.14	3.30	3.83	4.89	7.0	7.4	8.2

of r_∞ on the initial pressure of *n*-pentane is similar to that found with the normal decomposition rate and is satisfied by the equation

$$r_\infty = 0.50 \times 10^{-2} p_0 + 2.75 \times 10^{-5} p_0^2.$$

The ratio of the uninhibited rate (r_0) to the fully inhibited rate (r_∞) gives the apparent chain length, and the variation of the latter with initial pentane pressure is given by the expression

$$\text{apparent chain length} = r_0/r_\infty = \frac{3.63 \times 10^{-2} p_0 + 7.33 \times 10^{-5} p_0^2}{0.50 \times 10^{-2} p_0 + 2.75 \times 10^{-5} p_0^2}.$$

The numerical values are given in Table V and, as observed by Hobbs and Hinshelwood (*loc. cit.*) for the decomposition of ethane, propane, and hexane, the apparent chain length decreases with increasing hydrocarbon pressure.

TABLE V.

Variation of apparent chain length (r_0/r_∞) with *n*-pentane pressure. Temperature, 530°.

<i>n</i> -Pentane pressure (mm.)	50	100	150	200	250	300	350	400	450	500
Apparent chain length ...	6.7	5.0	4.8	4.7	4.6	4.3	4.2	4.1	4.0	3.9

r_∞ is much more nearly proportional than r_0 to $[p_0^2]$, which means that the decrease in apparent chain length with increasing initial pressure occurs nearly in accordance with an expression of the form

$$r_0/r_\infty = A + \frac{B}{p_0}, \text{ where } A = 3.8 \text{ and } B = 150.$$

Influence of Temperature.—A series of measurements made over the range 508—580° gave an approximate value of 76 kcal./g.-mol. for the activation energy of the fully inhibited decomposition.

ANALYTICAL RESULTS.

Analysis of Products.—An analysis was made of the products from the decomposition of 400 mm. of *n*-pentane in the presence of 10 mm. of nitric oxide at 530°. The combined materials from about 40 runs with $\Delta p/p_0 = 0.5$ were used. A second analysis was made of the lighter fraction only. The results are given in Table VI.

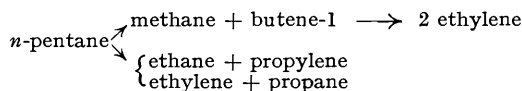
TABLE VI.

Analysis of products of decomposition of 400 mm. of n-pentane with 10.0 mm. of nitric oxide, at 530°. $\Delta p/p_0 = 0.5$.

	% by volume of total gas. Analysis 1.	Amount relative to CH ₄ = 1.0.	
		Analysis 1.	Analysis 2.
Hydrogen	1.0	0.1	0.1
Methane	8.3	1.0	1.0
Ethane	16.5	1.9	2.0
Ethylene	12.3	1.3	1.5
Propane	0.9	0.1	0.1
Propylene	15.7	1.8	1.9
Butylene	4.8	0.6	—
Pentane	40.4	4.9	—

DISCUSSION.

The analytical results are in moderate agreement with what would be expected on the basis of a molecular rearrangement process of the kind described for *n*-hexane (Partington and Danby, *loc. cit.*)



Assuming that the butene-1 undergoes some decomposition to give 2 molecules of ethylene, the amount from this source would be

$$\begin{aligned}
 & 2 \times \text{amount of butene-1 decomposed} \\
 & = 2 \times (\text{amount of methane found} - \text{amount of butene-1 found}) \\
 & = 2 \times (8.3 - 4.8) = 7.0\%.
 \end{aligned}$$

Thus, of the ethylene found, $(12.3 - 7.0)\% = 5.3\%$ is from the primary process. The propane figure is low, although the propylene and ethane percentages are in fair agreement.

The relative probability of cleavage in the pentane molecule in positions (1) and (2) will be given by

$$\text{methane : (ethane + propane)}$$

With the mean of the values (*propane found*) and (*ethylene from primary process*) taken to represent the true propane value, the ratio is

$$8.3 : \left(16.5 + \frac{0.9 + 5.3}{2} \right) \text{ or } 8.3 : 19.6.$$

Although there is some possibility that the residual pentane contained some other dissolved substances (C₃ and C₄) it is unlikely that any methane or ethane remained dissolved. Thus, independently of the propane value, the preference for a break in position (2) must be at least 16.5 : 8.3 or about 2 : 1.

Further, when the molecule breaks in position (2) the formation of ethane and propylene is definitely more probable than the alternative formation of ethylene and propane [cf. the break in position (2) for *n*-hexane].

REACTION KINETICS.

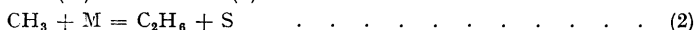
The fully inhibited reaction depends upon the initial pressure according to the equation

$$r = 0.50 \times 10^{-2} p_0 + 2.75 \times 10^{-5} p_0^2.$$

For certain values of p_0 the influence of the first term is small and the overall behaviour approximates over a limited range to that of a second-order change. If the inhibited process does in fact correspond largely to a residual molecular rearrangement reaction, then this, in the pressure range investigated, is still dependent on the rate of activation by collision.

The interpretation of the details of the chain mechanism is somewhat complex. With ethane the most probable mechanism seems to be a first-order primary decomposition into radicals, which can be removed either by reaction with nitric oxide, or by combination, largely in ternary collisions, but partly in binary collisions.

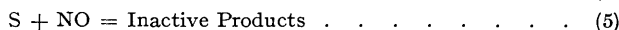
With the higher hydrocarbons a further possibility is present. The initial decomposition can yield a large radical which is itself susceptible of thermal decomposition. For example, with *n*-pentane we could well have



Other alternatives involve the formation of H or C_2H_5 , but (1), (2), and (3) may be taken as representative.

The radicals chiefly removed by the nitric oxide may be either CH_3 or the heavy radical S. In the latter case it can be shown that the nitric oxide inhibition curves will become independent of the hydrocarbon pressure as found by Hobbs for the decomposition of diethyl ether (*Proc. Roy. Soc.*, 1938, *A*, **147**, 456).

If to equations (1) to (3) are added



the usual stationary state calculation gives

$$\text{rate} \propto [\text{pentane}] \phi[\text{NO}]$$

From this it follows that

$$(\nu - \nu_\infty)/(\nu_0 - \nu_\infty) = \phi'[\text{NO}]$$

and is independent of [M].

Since in fact the value of γ is nearly the same for ethane as for pentane, there is no good reason for supposing that the importance of the reaction between nitric oxide and the larger radicals is markedly greater with pentane. Thus the reaction with the smaller radicals still plays an important part.

In the absence of nitric oxide the chain length diminishes as the pressure of pentane increases, and we may therefore assume that the chains are largely ended by a process involving a pentane molecule as has already been suggested for ethane.

The difference between ν_0 and ν_∞ which gives the rate of the repressible chain reaction is more nearly of the first order than ν_0 or ν_∞ themselves, a fact which is consistent with the fall in apparent chain length as the initial pressure rises. In fact the difference increases according to a power of the pentane pressure slightly greater than the first. This result is in agreement with that found for ethane, where it was concluded that an initiation process of order x combined with a radical recombination process of an apparent order y in ethane to give an overall dependence on ethane pressure of $[C_2H_6]^{1+x/2+y/2}$. x was found to be unity, and y about 0.66. This means an apparent order of 1.17 over the range studied.

The mechanism of the pentane chain reaction seems therefore to be generally similar to that of ethane.

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