453. *The Thermal Decomposition of* n-*Hexane.*

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The thermal decomposition of *n*-hexane has been further investigated.

On the basis of the hypothesis that the nitric oxide-inhibited reaction represents a molecular reaction, the relative probabilities for the initial rupture of the chain at various links are $C_{1-2} : C_{2-3} : C_{3-4} : : 3{\cdot}9 : 2{\cdot}5 : 1$. When the C_{2-3} break occurs the chances are more than 10 : 1 that ethane and butene-1 will be formed rather than ethylene and butane.

The total analysis of the products is consistent with the measured rates of the primary and of various consecutive reactions.

Various problems connected with the thermal decomposition of hydrocarbons must still be regarded as incompletely solved. Among them are the following : (*a*) the question whether the residual reaction measurable when the rate has been reduced to a limiting value by added nitric oxide represents a molecular reaction or some kind of chain reaction which persists in spite of the inhibitor, (*b*) the modes of breaking of the hydrocarbon chain in the primary process. It is proposed to subject these matters to some further experimental study. The present paper deals with *n*-hexane.

Among previous studies on *n*-hexane are those of Dintzes and Frost (*J. Gen. Chem. Russia*, **1933**, **3**, 747) made, however, before the chain mechanism had been established, and of Hobbs and Hinshelwood (*Proc. Roy. Soc.*, **1938**, *A*, **167**, 447), which was of a summary character only, the behaviour of hexane being compared with that of several other hydrocarbons in respect of apparent chain length. The theoretical considerations of Kossiakoff and Rice (*J. Amer. Chem. Soc.*, **1943**, **65**, 590) should be mentioned in this connexion, as also should a detailed experimental study by Steacie and Folkins on the decomposition of *n*-butane (*Canadian J. Res.*, **1940**, **18***B*, **1**).

EXPERIMENTAL.

(i) *Determination of Decomposition Rate.*—The hexane was decomposed in a silica bulb of about 250 c.c. capacity maintained at a constant temperature in an electric furnace. It was connected to a capillary mercury manometer, to storage vessels for reactants, and to the usual system of high-vacuum pumps. Temperatures were measured by a platinum–platinum-rhodium thermocouple and potentiometer. To prevent condensation of hexane, the connecting tubes and manometer were wound with resistance wire and electrically heated. The reaction was followed by measurements of pressure change. The pressure–time readings were plotted, and the exact initial pressures and initial rates obtained from the graph by extrapolation and tangent-drawing respectively.

(ii) *Analysis of Reaction Products.*—For the collection of samples of product the apparatus was provided with a Toepler pump by which the contents of the reaction vessel could rapidly be withdrawn. When the hexane in the reaction vessel had decomposed to a given extent, as indicated by the pressure change, the gases were removed for analysis. By combining the products from about 50 separate experiments some 2—3 c.c. of condensed material (including unchanged hexane) were obtained.

The products from the decomposition of hexane may potentially contain all the straight-chain paraffin and olefin hydrocarbons having six carbon atoms or less, together with hydrogen. To carry out a complete analysis of such a mixture by low-temperature fractional distillation would be difficult and would require considerable quantities of material. Fractionation was therefore only employed to separate the mixture into a series of fractions having b. p.s separated by about 40°, each of which was then further investigated by other methods.

The products withdrawn from the reaction bulb by means of the Toepler pump were passed through two traps cooled with liquid air. The uncondensed fraction (consisting of methane with a little hydrogen) was collected in an evacuated bulb of known volume. The total amount of this fraction was determined by measuring its temperature and pressure. A sample was then taken from it for analysis by means of a Bone and Wheeler apparatus, the hydrogen being determined by oxidation over copper oxide at 275°, and the methane by combustion with excess of oxygen. The condensed fractions in the traps were combined and transferred by distillation to the still-pot of a glass low-temperature distillation apparatus. The column was of 8-mm. internal diameter and about 60 cm. long and was packed with rings of stainless-steel gauze. The reflux condenser consisted of a pointed copper rod which was passed into the upper part of the column through a rubber joint and was cooled by the introduction of liquid air, solid carbon dioxide and acetone, or freezing mixtures into a lagged metal cup soldered to its upper end. The temperature of the rod was measured by means of a copper–constantan thermocouple soldered to it. The whole column was contained inside a glass jacket which was continuously evacuated. The column was provided with a manometer, and distillations were carried out at atmospheric pressure.

The reflux condenser was first cooled with liquid air and the column operated under total reflux until the packing was thoroughly wetted, the still-pot being warmed, as required, by a small electric heater.

The temperature of the reflux condenser was then raised and three fractions were taken off successively. These were: ethylene and ethane (b. p.s −104° and −89°), propylene and propane (b. p.s −48° and −42°) and butene-1 and butane (b. p.s −6° and −1°). The fractions were collected in a trap cooled in liquid air and were distilled into separate bulbs of known volume, where their temperature and pressure were measured. Samples were taken from each fraction, and the ratio of saturated to unsaturated hydrocarbon determined in the Bone and Wheeler apparatus. (Concentrated sulphuric acid containing silver sulphate was used as an absorbent for ethylene, 87% sulphuric acid for the higher olefins.) The residue in the still-pot (consisting of unchanged hexane together with traces of C_5 and C_4 hydrocarbons which had not been separated) was distilled into a weighed tube closed by a tap and its amount determined by direct weighing. This fraction was analysed by adsorption on a charcoal column and fractional desorption with amyl acetate vapour by a technique derived from that of Claesson (*Arkiv Kemi Min. Geol.*, 1942, **15**, *A*, 1; The Svedberg Mem. Vol., 1942, p. 82). This analysis was carried out by Mr. C. S. G. Phillips, who is engaged upon a general study of the method. From a knowledge of the total amount and composition of each fraction the complete analysis of the product was calculated.

Considerable modifications in the distillation apparatus and technique were made as the result of trial analyses. A series of experiments was also made with synthetic mixtures, from the results of which a correction could be made for the fact that under the standard conditions used the unsaturated hydrocarbon in a saturated–unsaturated mixture was incompletely adsorbed by the reagent. With the method finally adopted the figures below were found in a trial analysis on a 5-component mixture of known composition.

	C.c. taken.	C.c. found.		C.c. taken.	C.c. found.
Ethylene	15	14	Butene-1	27	27
Ethane	17	17	Butane	14	14
Propane	27	28			

Experimental Results.—*Influence of nitric oxide.* An investigation was made of the dependence of the initial rate of decomposition on the pressure of added nitric oxide. With 95 mm. of *n*-hexane at 570° the initial rate fell to a steady limit reached with about 12 mm. of nitric oxide. The ratio of the rate of decomposition in the absence of nitric oxide to the limiting rate was 1·75 (Table I).

TABLE I.

Influence of nitric oxide.

95 Mm. of *n*-hexane; 570°.

Pressure of NO (mm.)	0	2·0	3·9	5·0	9·3	11·5	16·0	20·0
Initial rate (mm./min.)	31·8	29·8	23·3	24·0	23·1	18·3	18·2	18·1
Initial rate (relative)	1·00	0·94	0·73	0·75	0·73	0·58	0·57	0·57

TABLE II.

Influence of hexane pressure.

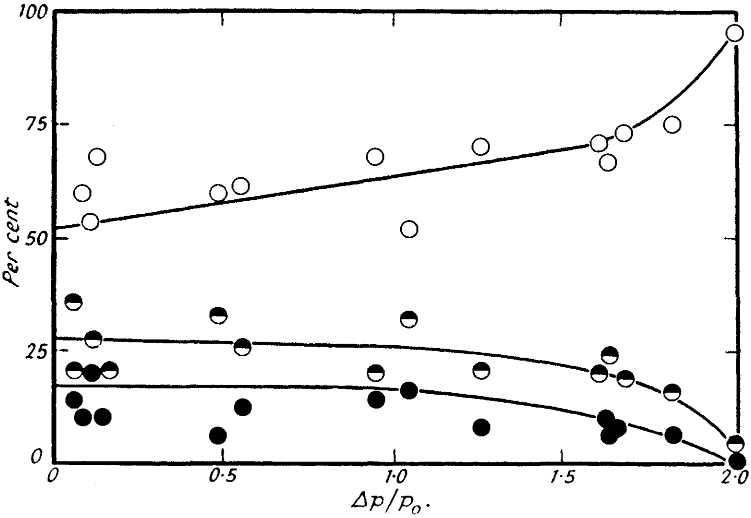
No nitric oxide present; 535°.

Initial press. of hexane (mm.)	3·4	7·2	25·0	34·0	46·0	94·0	108·3	115	144	171
Initial rate (mm./min.)	0·08	0·3	2·1	2·9	5·8	9·1	11·3	13·7	16·5	22

15 Mm. of nitric oxide; 536°.

Initial press. of hexane (mm.)	15·5	20·0	33	48·5	60	133	151	184
Initial rate (mm./min.)	0·18	0·22	0·39	0·62	1·0	3·2	3·8	6·8

Influence of initial pressure of n-*hexane.* The influence of the initial pressure on the initial rate of decomposition, both without nitric oxide and with 15 mm., is shown in Table II. A logarithmic plot revealed that in the absence of nitric oxide the initial rate was directly proportional to the initial pressure over the range 30—180 mm. Below 20 mm., however, the first-order rate constant falls off. With 15 mm. of nitric oxide the initial rate varied with (initial pressure of *n*-hexane)$^{1·5}$.



○ = *Saturated hydrocarbons.*
◓ = *Ethylene.*
● = *Higher olefins.*

The rate constants are expressed by the relations

$$k = \left(\frac{\mathrm{d}v_0}{\mathrm{d}p_0}\right)_{p_0 = 100\text{ mm.}} \qquad \text{where } v_0 = \left(\frac{\mathrm{d}(\Delta p)}{\mathrm{d}t}\right)_{\Delta p = 0}$$

Influence of temperature on the initial rate of decomposition. Measurements were made, with and without nitric oxide, of the initial rate of decomposition over the temperature range 500—620°. At each temperature measurements were made at three different initial pressures (50, 100, and 150 mm.). The results are shown in Table III. From the graph of ln ($k \times 10^3$) against $10^3/T$, it was found that for the decomposition of *n*-hexane in the absence of nitric oxide:

$$\ln k = 33·4 - (56·8 \times 10^3)/RT$$

and for the decomposition in the presence of 15 mm. of nitric oxide:

$$\ln k = 42·9 - (74·0 \times 10^3)/RT$$

k is in min.$^{-1}$, R in g.-cals./mol./°c.

Analysis of Products.—A survey was first made of the way in which the ratio of ethylene to higher olefins (propylene + butene) in the products varied with the extent of the decomposition and with the temperature. For these analyses the gases from the reaction vessel were withdrawn through a trap cooled to 0° into vessels from which they could be transferred to the Bone and Wheeler apparatus. The results are shown in the figure. Although not of great accuracy, they showed that the composition of the products taken when $\Delta p/p_0 = 0·5$ would approximate to the composition at zero decomposition. Moreover, the composition of the products was not seriously affected by temperature or by the addition of the nitric oxide.

Four separate analyses were made of the products from the decomposition of 200 mm. of *n*-hexane in the presence of 10 mm. of nitric oxide at 530°, the combined material from about 50 runs with $\Delta p/p_0 = 0·5$ being taken in each case. The results are shown in Table IV.

TABLE III.

Influence of temperature.

Series 1.						
Temp., °c.	502	515·5	554·5	579·5	603·5	618·5
$k \times 10^3$ (min.$^{-1}$) at 100 mm. initial pressure :						
without NO	32	52	260	830	1960	2400
with 15 mm. NO	2·6	10·0	135	460	1300	1840
Series 2.						
Temp., °c.	512	534	535·5	571·0	588	
$k \times 10^3$ (min.$^{-1}$) with 15 mm. NO	11	25	23	290	650	

TABLE IV.

Uncorrected analyses (% *by vol.*).

					Mean.
Hexane	51·6	49·7	39·5	40·6	45·4
Butane	0·9	0·5	0·3	0·6	0·6
Butene	2·4	2·4	6·4	3·2	3·6
Propane	1·8	1·7	1·8	1·5	1·7
Propylene	5·6	11·9	14·2	13·3	11·2
Ethane	8·2	5·4	6·6	10·9	7·8
Ethylene	14·0	13·5	19·0	15·7	15·5
Methane	—	—	(11·1)	13·2	13·2
Hydrogen	—	—	0·7	0·9	0·9
Methane + hydrogen	15·5	14·9	11·8	14·1	14·1

During the distillation it was difficult to judge when all the C_4 fraction had come off. The residue was therefore analysed by the fractional desorption method referred to above. Mr. Phillips's results were as follows :

Residue contained:

C_6 compounds .... 89·3% of total C_5 compounds ...... 2·1% C_4 compounds .... 8·6%.

When account is taken of these results and the superior accuracy of the third and fourth fractionations allowed for, the figures for the composition of the products are as follows :

Component.	% by vol.	Component.	% by vol.
Hexane	39·7	Propylene	12·2
Pentene	1·0	Ethane	7·8
Butane	0·6	Ethylene	15·5
Butene	7·4	Methane	13·2
Propane	1·7	Hydrogen	0·9
			100·0

In making the correction the C_4 fraction found in the desorption experiment was taken to be butene, since the proportion of butane in the main fraction was extremely small. The C_5 fraction was taken to be pentene, pentane being very unlikely on chemical grounds.

DISCUSSION.

The inhibition by nitric oxide of the decomposition of *n*-hexane indicates that free radicals play a part in the mechanism of the reaction. The value of 1·75 obtained for the mean chain length at 570°, and for an initial pressure of 95 mm., is in fair agreement with other values obtained by Hobbs and Hinshelwood.

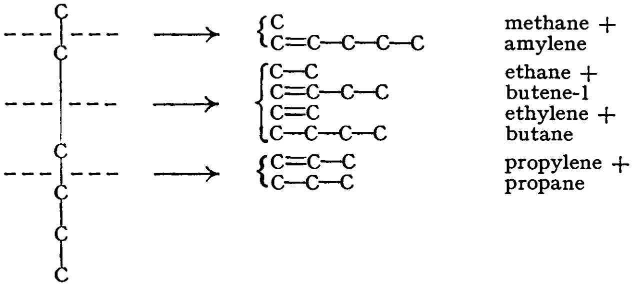
Mean chain length and temperature. The values obtained in this investigation for the energy of activation of the decomposition at 100 mm. initial pressure were :

for the normal decomposition, 58·8 kcals./mol.
for the inhibited reaction, 74·0 kcals./mol.

The fact that these differ means that the mean chain length is dependent on temperature, the values showing that it increases as the temperature falls. This general effect (the dependence of mean chain length on temperature) has been discussed by Staveley and Hinshelwood (*J.*, 1937, 1568). The uninhibited *n*-hexane decomposition is approximately of the first order.

The observation that the rate of the fully inhibited reaction varies approximately as $(p_{\text{hexane}})^{1\cdot5}$—which is in agreement with the finding of Hobbs and Hinshelwood—is a result which must be explained. There is no evidence that the 1·5 power law is valid over a wide range, and it may merely be an approximation for the transition from the first order to second order with falling pressure which would be observed if the residual reaction were unimolecular and if the chains were all suppressed. On the other hand, a tentative suggestion was considered by Hobbs and Hinshelwood, namely, that the residual inhibited reaction could itself depend on a special type of chain reaction with carriers immune to the attack of nitric oxide. Steacie and his associates have, in fact, found that the decomposition of *n*-butane (which is theoretically very similar to that of *n*-hexane) could be initiated at low temperatures by free radicals from ethylene oxide, and that the sensitization persisted in the presence of large amounts of nitric oxide, showing that in this case the fully inhibited decomposition did not correspond to the complete suppression of chains.

Analytical results. In discussing the analytical results we shall, however, assume in the first instance that the steady rate attained in presence of the nitric oxide represents a reaction at least sufficiently free from chains to afford information about the primary positions of breaking of the hexane molecule. According to what was said above, the first step in the decomposition will be the rupture of one of the C–C bonds, leading to a rearrangement to a saturated and an unsaturated hydrocarbon. It was found by infra-red absorption of product samples that all the unsaturated hydrocarbons present had terminal double bonds, so there remain the following possible modes of rupture of the hexane molecule :



Preliminary measurements, including infra-red absorption, showed that the initial products contained ethylene, propylene, and butene-1, and that the proportions at the stage where $\Delta p/p_0 = 0{\cdot}5$ approximate to those at zero decomposition. They showed, moreover, that the formation of these three unsaturated hydrocarbons was in a large measure by simultaneous rather than by consecutive reactions.

In order, however, to be able to interpret the full analyses in more detail, auxiliary measurements were made of the rates of decomposition of the various product species. The results are given in Table V.

TABLE V.

Relative reaction rates of possible subsequent decompositions (approximate).

	$k \times 10^4$ (min.$^{-1}$) for fully inhibited reaction.	Apparent order of reaction over (limited) range studied.
Ethane	6	—
Propane	24	1·5
Butane	180	1·5
Pentane	240	1·4
Ethylene	(5) (polymerisation)	—
Propylene	18	1·6
Butene-1	210	1·5
Cf. *n*-hexane	250	1·4

Unfortunately, no pentene-1 was available, but from the results for propylene and butene-1 it is reasonable to assume that the value for *k* would be of the order of 10 times that for *n*-hexane; it was also assumed for the purposes of calculation that the decomposition of all these substances was of the order 1·5.

Neglecting the small amount of hydrogen, we may now consider the following scheme :

$$\begin{tikzcd}
\text{methane + pentene-1} \arrow[r] & \text{ethylene + propylene} \\
\text{hexane} \arrow[u, "(1)"] \arrow[r, "(2)"] \arrow[d, "(3)"] & \left\{\begin{array}{l}\text{ethane + butene-1} \longrightarrow \text{2 ethylene}\\ \text{ethylene + butane} \longrightarrow \text{products}\end{array}\right. \\
\text{propane + propylene} &
\end{tikzcd}$$

From the results in Table V it may be taken that during the time of the experiment the methane, ethane, ethylene, propane, and propylene did not undergo further change. The butene-1 and pentene-1 undoubtedly undergo some further decomposition. The case of butane is doubtful. A very rough estimate of the amount of decomposition undergone by the butane may be obtained as follows :

Initial pressure of *n*-hexane	200 mm.
Final pressure of mixture	300 mm.
% Hexane in final mixture	40 (by analysis)
∴ Pressure of hexane	120 mm.
∴ Amount of hexane decomposed	80 mm.

Now the average pressure of butane was $\frac{\frac{1}{2} \times 0{\cdot}6}{100} \times 300 = 0{\cdot}9$ mm.

If the average pressure had been 200 mm., the amount decomposed would have been approximately 80 × 180/250. Thus the actual amount of decomposition would be of the order

$$80 \times \frac{180}{250} \times \left(\frac{0{\cdot}9}{200}\right)^{1{\cdot}5} = 0{\cdot}016 \text{ or } < 0{\cdot}01\%.$$

It can therefore be assumed that the butane does not decompose appreciably during the experiment.

The decomposition of the pentene-1 is very important and very nearly keeps pace with the formation, so that the ethylene and propylene into which it breaks down count practically, from the analytical point of view, as primary products. The amount of pentene-1, had there been no decomposition, should have been equivalent to the amount of methane, *i.e.*, 13·2%. But the amount found was 1·0%. Thus the amount decomposed = 13·2 − 1·0 = 12·2%. This should also be given by (propylene found − propylene equivalent to propane) = 12·2 − 1·7 = 10·5%.

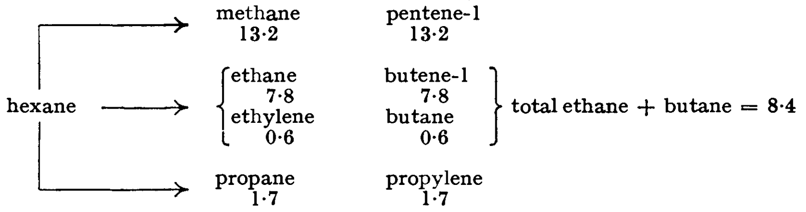
According to the rate measurements, the amount of butene-1 which decomposes should be approximately :

$$80 \times \frac{210}{250} \times \left(\frac{3{\cdot}7}{200}\right)^{1{\cdot}5} = 0{\cdot}17 \text{ or } 0{\cdot}06\%.$$

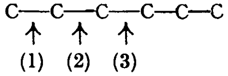
Thus the butene-1 analysis should give about 7·4 + 0·1 = 7·5, which agrees fairly closely with the value of 7·8 found for ethane.

The ethylene present should be the sum of the following : 0·6 from that equivalent to the butane, 0·2 from the decomposition of butene-1, and 12·2 from the decomposition of pentene-1, *i.e.*, 13·0. The propylene should equal 12·2 from the pentene + 1·7 from that equivalent to the propane = 13·9. This scheme, with the observed reaction rates of these, leads to the analytical figures shown in the upper row of figures in the following table, whereas the lower row gives the observed figures, which are in fair agreement. On this basis, the primary products would appear to be as follows :

CH_4.	C_2H_6.	C_3H_8.	C_4H_{10}.	C_2H_4.	C_3H_6.	C_4H_8.	C_5H_{10}.
13·2	7·8	1·7	0·6	13·0	13·9	7·4	1·0
13·2	7·8	1·7	0·6	15·5	12·2	7·4	1·0



The chances of the hexane molecule breaking in positions (1), (2), and (3) would thus appear to be in the ratio 13·2 : 8·4 : 2 × 1·7, or 3·9 : 2·5 : 1, the figure relating to position (3) being



doubled to allow for the fact that reactions at positions (1) and (2) have each two chances to contribute to the products. When the chain breaks in position (2) the chances are more than 10 : 1 that ethane and butene-1 will be formed rather than ethylene and butane.

Further comment and discussion is reserved until further experimental studies have been completed.

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