LVI.—*The Mechanism of Thermal Decomposition of the Normal Paraffins.*

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SINCE Berthelot (*Compt. rend.*, 1866, **62**, 905) put forward his well-known theory regarding the mode of decomposition of hydrocarbons by heat, in which acetylene played the most important part as an early product of degradation and as " générateur fondamental des carbures pyrogenés," the literature relating to the subject has become extensive, and several attempts have been made to evolve a theory which will embrace all the observed facts, which Berthelot's does not.

Of the more important observations must be mentioned those of Thorpe and Young (*Proc. Roy. Soc.*, 1871, **19**, 370), Haber (*Ber.*, 1896, **29**, 2691), Bone and Coward (J., 1908, **93**, 1197), Davidson (*J. Ind. Eng. Chem.*, 1918, **10**, 901), and Calingaert (*J. Amer. Chem. Soc.*, 1923, **45**, 130).

Thorpe and Young distilled solid paraffins under pressure, obtaining mixtures of liquid paraffins and olefins which led them to suggest a general reaction involving a simultaneous formation of hydrides and olefins ; according to this, the primary decomposition of butane would be $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 = CH_3{\cdot}CH_3 + CH_2{:}CH_2$.

Haber examined *n*-hexane, in particular, and found that between 600° and 800° the primary decomposition involved the elimination of methane, leaving one of the next lower olefins, C_5H_{10}.

Bone and Coward, from the action of heat on methane, ethane, ethylene, and acetylene, concluded that methane was the most stable and was always a principal product of decomposition of the others, particularly above 800°, when one of the main reactions was the hydrogenation of such residues as $\vdots CH$, $:CH_2$, and $\cdot CH_3$ (which might have momentary separate existence).

Davidson, continuing work by Zanetti (*J. Ind. Eng. Chem.*, 1916, **8**, 674, 777), studied the " cracking " of the ethane–propane fraction of natural gas, paying particular attention to the formation of aromatic hydrocarbons, which were accompanied by olefins and diolefins. Acetylene was absent, though the temperature used was insufficient to decompose it had it been formed. Arguing on the results of experiments by Jones (J., 1915, **107**, 1582), Davidson concluded that the aromatic hydrocarbons were produced by condensation of the olefins, with elimination of hydrogen.

Calingaert attempted to determine the initial stage in the decomposition of *n*- and *iso*-pentane, limiting the temperature to 600°. The results suggested that with *n*-pentane for the most part the carbon chain was ruptured in such a manner as to give an ethyl and a propyl group, one of which was then saturated at the expense of the other, yielding either (*a*) ethane and propylene or (*b*) ethylene and propane. To a certain extent, methyl and butyl groups could be formed, yielding methane and butylene.

From our own study of the action of heat on the unbranched-chain paraffins, from ethane to *n*-hexane, we conclude that the primary decompositions can be represented by series of equations indicating the rupture of the chain at any position, with the production of an olefin and the complementary lower paraffin or, at the limit, hydrogen. Thus with ethane, propane, and *n*-butane we have found the primary decompositions to be :

Ethane : (i) $CH_3{\cdot}CH_3 = CH_2{:}CH_2 + H{\cdot}H$.
Propane : (i) $CH_3{\cdot}CH_2{\cdot}CH_3 = CH_2{:}CH_2 + CH_3{\cdot}H$,
(ii) $CH_3{\cdot}CH_2{\cdot}CH_3 = CH_3{\cdot}CH{:}CH_2 + H{\cdot}H$.
n-*Butane :* (i) $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 = CH_2{:}CH_2 + CH_3{\cdot}CH_2{\cdot}H$,
(ii) $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 = CH_3{\cdot}CH{:}CH_2 + CH_3{\cdot}H$,
(iii) $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 = CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 + H{\cdot}H$.

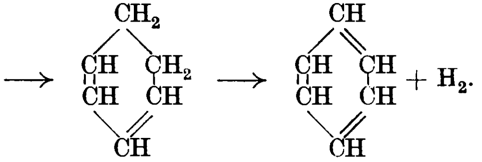
With each hydrocarbon, the reactions are given in order of their importance. As the series is ascended, the tendency for hydrogen to be eliminated, leaving an olefin with the same number of carbon atoms as the original paraffin, rapidly diminishes.

Equations (i) and (ii) for propane have recently been suggested, as conforming with the results of their experiments, by Pease (*J. Amer. Chem. Soc.*, 1928, **50**, 1779) and Frey and Smith (*J. Ind. Eng. Chem.*, 1928, **20**, 948), who have also suggested equation (i) for ethane. Of the four possible equations for *n*-pentane, Calingaert (*loc. cit.*) noted the first three.

Following these primary decompositions, many complicated reactions occur during " pyrosynthesis " at the same or higher temperatures. With ethane, for example, at temperatures above 700°, the hydrogenation of fugitive " residues," $:CH_2$, as suggested by Bone and Coward (*loc. cit.*), would seem to occur. At comparatively low temperatures, subsequent to the formation of ethylene, butadiene is produced from each of the paraffins (compare Norton and Andrews, *J. Amer. Chem. Soc.*, 1886, **8**, 1). Above the range 700—750°, under the conditions of our experiments, benzene and other aromatic hydrocarbons are produced from each gas (methane included). At this stage of the syntheses, ethylene appears to be the starting point. Our experiments show that ethylene readily polymerises to butylene which, by elimination of hydrogen, yields butadiene. From the presence of six-membered unsaturated hydrocarbons (liquids, b. p. 59° and 78°) amongst the synthetic products from the paraffins, we conclude that the butadiene reacts with ethylene (compare Jones, *loc. cit.*), the suggested mechanism being :

(*a*) $\mathrm{CH_2{:}CH_2 + CH_2{:}CH_2 \longrightarrow CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 \longrightarrow}$
$\mathrm{CH_2{:}CH{\cdot}CH{:}CH_2 + H_2}$.

(*b*) $\mathrm{CH_2{:}CH{\cdot}CH{:}CH_2 + CH_2{:}CH_2 \longrightarrow}$ *either*
$\mathrm{CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2}$ *or* $\mathrm{CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH_2 + H_2}$



Further, by analogy with the formation of diphenyl from benzene, it is reasonable to suppose that butadiene can condense with benzene, hydrogen being eliminated, to form naphthalene ; and that anthracene and phenanthrene can be formed from the naphthalene in a similar manner.

The first member of the series, methane, requires separate consideration. Although the absence of a C—C linkage causes its behaviour to be different from that of the higher members, its decomposition point being about 200° higher than that of ethane, whereas there is but a 25° interval between the decomposition points of the others, yet liquid hydrocarbons in quantity are produced from methane, the formation of benzene being at its optimum over the range 1000—1100°.* As Bone and Coward (*loc. cit.*) have shown, the main decomposition of methane is ultimately to carbon and hydrogen. At comparatively low temperatures, however, ethylene is formed. As with other paraffins, we regard this ethylene as the source, through butadiene, of the benzene and other aromatic hydrocarbons produced. The mechanism of the early decomposition may be expressed by $\mathrm{CH_3{\cdot}H \longrightarrow {:}CH_2 + H{\cdot}H}$, two of the $\mathrm{CH_2}$ residues, of fugitive existence as postulated by Bone and Coward, combining to form ethylene.

With regard to our suggested mechanism of the primary decompositions of the paraffins possessing a carbon chain, Professor T. M. Lowry has pointed out to us an analogy with the mechanism of reversible isomeric changes which he has been good enough to outline in an addendum to this paper.

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* In the publication of these observations we have been anticipated by Fischer (*Brenn. Chem.*, 1928, **9**, 309), whose method of experiment has been almost identical with our own. We confirm his results in all important particulars.

EXPERIMENTAL.

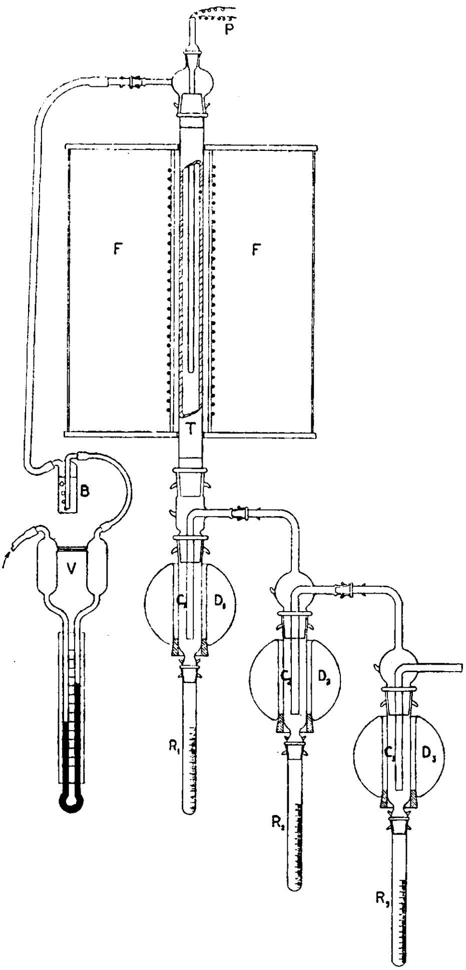
The Hydrocarbons.—Methane was obtained from a blower of firedamp at a coal-mine in South Wales. The firedamp contained no other inflammable gas, but some nitrogen and carbon dioxide were present. The methane was purified by liquefaction. Our main supplies of ethane, propane, and *n*-butane were obtained compressed from America, where they had been fractionated from natural gas. They were already of a high degree of purity, but in each instance they were liquefied and fractionated before use. Check experiments were made with propane and *n*-butane prepared by the Grignard reaction, liquefied, and fractionated. The purity of the gases was tested by their boiling points and by explosion analyses. The liquid hydrocarbons, *n*-pentane and *n*-hexane, were obtained from as pure a source of supply as possible and fractionated many times to ensure that only the unbranched-chain paraffin was present. The purity of the final products (the yields of which were often poor) was checked by density determinations.

Method of Experiment.—With each hydrocarbon three types of experiment were made : (1) *static* ; (2) *circulation* ; and (3) *stream*, in which large volumes of each gas were passed at a constant rate through a tube of quartz heated at a constant temperature, the liquid and gaseous products of decomposition being collected. Only the " stream " experiments need be described.

Stream Experiments.—The apparatus used is shown diagrammatically in Fig. 1. The gas was passed through a Venturi meter, V, and a bubbler, B, to the upper end of the reaction tube, T, which was supported vertically within an electric furnace, F. The reaction tube was 70 cm. long and of 2·2 cm. internal diameter. A narrow quartz tube, P, with its lower end closed so as to form a pocket for a thermocouple, was arranged axially within the reaction tube. On issuing from the reaction tube, the gases passed through three condensers, C, in series, cooled by solid carbon dioxide dissolved in ether, contained in Dewar vessels, D. Attached to the bottom of each condenser were graduated receivers, R. Ground joints were used throughout the apparatus.

In carrying out an experiment, a stream of nitrogen was passed through the apparatus until all air had been swept out. Connexion was then made to the supply of hydrocarbon, the rate of flow of which was adjusted to 4 litres per hour. In each experiment, from 12 to 16 litres of gas were passed. The resultant gases, after passing through the condensers, were either bubbled through bromine water or, at the end of the first hour, collected in a gas holder for analysis, their volume being measured. At the conclusion of an experiment, the stream of hydrocarbon was replaced by one of nitrogen, and the furnace allowed to cool. The condensers were disconnected, stoppered, and gently warmed so as to allow their frozen contents to melt and flow into the graduated receivers, which were then removed and stoppered.

Fig. 1.



The liquid products of decomposition were weighed and distilled over different temperature ranges. In recording the results, the fraction boiling at a low temperature (mainly between 80—90°) is referred to as the " benzene fraction." It contained 85—95% of benzene, with, at the lower temperatures of decomposition, some unsaturated hydrocarbons. The gaseous products were analysed and in some experiments liquefied, with subsequent fractionation. In other experiments they were brominated. Records were kept of the amount and character of the carbon deposited within the reaction tube, which was thoroughly cleaned by burning out between successive experiments.

When a liquid paraffin was used, the procedure was modified slightly, the liquid being run directly into the reaction tube by allowing it to trickle down the thermocouple sheath, the rate of flow (0·166 g.-mol. per hour) being comparable with the rate of 4 litres per hour used for the gases.

Gas Analysis.—Owing to the complexity of the mixtures obtained at temperatures below 750°, accurate gas analyses often could not be made. The higher paraffins, propane in particular, are soluble in some of the reagents used for estimating other constituents, whilst ethylene, when present in high concentration, is appreciably soluble in the ammoniacal silver chloride used for estimating acetylene. When comparing the analyses, the fact that some ethylene is recorded as "acetylene" should be borne in mind. In some of the experiments at the lower temperatures the gases were brominated, the bromides fractionated under reduced pressure, and the unsaturated hydrocarbons regenerated by means of a zinc–copper couple, according to the scheme suggested by Manning, King, and Sinnatt (Fuel Research Board, Tech. Paper No. 19, 1928). The products of decomposition above 750° did not present any difficulty, since the unsaturated hydrocarbons were much diluted with methane and hydrogen and the higher paraffins had been mostly decomposed.

Results of Experiments.—The results obtained from the "stream" experiments with each hydrocarbon are summarised in the tables that follow, the percentages of total liquids, "benzene" fraction, and carbon being given by weight, and others by volume.

TABLE I.

The Decomposition of Methane.

					Gas analyses, % (by vol.).			
Temp.	Increase in vol., %.	Total liquids, %.	Benzene fraction, %.	C, %.	Higher olefins.	C_2H_4.	H_2.	CH_4.
900°	—	1·2	—	—	0·6	2·8	14·0	82·6
950	3·7	2·0	1·1	Trace	0·9	3·7	31·5	63·9
1000	16·6	3·7	3·2	1·4	0·4	2·8	42·6	54·2
1050	27·5	2·6	1·7	4·5	0·3	2·1	54·3	43·3

Methane (see Table I). At 1000°, crystals of naphthalene were formed. The gaseous products of decomposition at 950° were brominated. Distillation of the bromides showed the presence of ethylene dibromide and butadiene tetrabromide. The liquids distilling below 170° for the most part (about 95%) boiled at 80° and were found to be benzene. A small quantity boiled between 76—80°. The liquids of high boiling point contained naphthalene and anthracene.

Ethane (see Table II). There were no liquid products at 700°,

TABLE II.

The Decomposition of Ethane.

					Gas analyses, % (by vol.).					
Temp.	Increase in vol., %.	Total liquids, %.	Benzene fraction, %.	C, %.	Higher olefins.	C_2H_2.	C_2H_4.	H_2.	CH_4.	C_2H_6.
700°	32·7	Nil	Nil	Nil	1·7	2·8	21·3	21·9	2·7	49·6
750	63·0	2·1	—	Trace	4·7	4·3	24·3	32·3	13·3	21·1
800	63·9	9·7	6·9	—	3·7	3·0	21·1	38·4	21·1	12·7
850	—	17·9	11·2	—	1·7	2·3	14·7	41·4	32·4	7·5
900	71·0	21·9	10·6	3·1	1·6	1·8	5·0	44·3	38·9	8·4
950	87·5	12·8	8·0	13·9	0·4	1·0	3·8	52·6	40·8	1·4
1000	109·0	6·5	3·6	16·2	0·3	0·8	2·4	58·5	33·9	4·1

whereas Williams-Gardner (*Fuel*, 1925, **4**, 430), working in these laboratories, obtained traces when using a much slower gas-stream (½ l. per hour). At 750°, a high proportion of the liquids obtained was found to be unsaturated. The gases were liquefied (by liquid air) and brominated, the white crystalline solid, m. p. 114°, obtained being proved to be butadiene tetrabromide. At 800°, crystals of naphthalene were deposited, and the gases contained butadiene. At 850°, the gases contained a small quantity of butadiene, whilst the liquids distilled mainly between 80—85°, and proved to be benzene. At 900°, the liquids contained much heavy oil, only about half distilling between 80—100°. At 950°, much naphthalene was formed, and more than half the liquid condensed was benzene.

As the temperature of decomposition was raised from 750°, the total yield of liquid products increased until a maximum was reached at 900°, the yield then representing 21·9% by weight of the ethane passed. The fraction of the liquids boiling between 80—90° was at a maximum for the decomposition at 850°. The liquids formed at 750° were chiefly unsaturated hydrocarbons, but the low-boiling fraction obtained at 850° and above was nearly pure benzene, the residual oil being composed chiefly of naphthalene and anthracene.

From the gas analyses and the volume changes, it will be seen that at 700° about 90% of the ethane that decomposed did so according to the equation $C_2H_6 = C_2H_4 + H_2$. As the temperature of decomposition was raised, the proportion of hydrogen formed continuously increased, whilst that of the ethylene reached a maximum and then rapidly decreased. Methane and the higher olefins, it would seem, are secondary products of decomposition, for the proportion of methane increased with rise of temperature to 950°, thereafter decreasing, and that of the higher olefins reached a maximum at 750°. Butadiene was found in the gases at 750°, 800°, and 850°.

It will be noticed that at no temperature did the ratio CH_4/H_2 in the products of decomposition in these "stream" experiments reach the high value 1·94 found by Bone and Coward (*loc. cit.*) on heating ethane in closed tubes, a result which, with other considerations, led them to postulate the transitory existence of unsaturated $\dot{\cdot}CH_2$ residues. We confirm the high value of this ratio when ethane is heated in closed tubes at 800° during ½ hour, and conclude therefrom that the formation of methane by the hydrogenation of $\dot{\cdot}CH_2$ residues (arising from the partition of the ethylene molecule) is a secondary reaction.

Propane (see Table III). The percentages of methane are minimum values, calculated from explosion analyses, after all but paraffins had been absorbed, on the assumption that only methane

TABLE III.

The Decomposition of Propane.

					Gas analyses, % (by vol.).				
Temp.	Increase in vol., %.	Total liquids, %.	Benzene fraction, %.	C, %.	Higher olefins.	C_2H_2.	C_2H_4.	H_2.	CH_4.*
700°	52·5	1·0	—	—	14·2	3·4	19·7	11·8	14·1
750	88·8	6·9	4·2	—	13·3	7·1	20·5	13·3	26·8
800	105·0	17·0	10·1	Trace	3·4	2·9	19·7	20·8	38·8
850	106·2	23·1	11·6	0·9	2·3	2·5	14·5	26·6	46·2
900	119·0	20·1	9·7	5·0	1·4	1·8	9·8	33·4	45·8
950	144·0	10·3	5·4	11·3	0·5	1·1	6·1	44·0	41·5
1000	159·0	5·5	2·2	18·3	0·5	1·1	5·8	51·3	36·1

* Minimum values.

and ethane (not recorded in Table III) were present. Actually, there was some undecomposed propane at the lower temperatures. A direct (rough) estimation of propane in the mixed paraffins from the decomposition at 700°, by absorption with absolute alcohol, showed them to contain about 30%. The figure for methane in that analysis should therefore be raised to about 20%.

At 750°, a mobile liquid was obtained, *d* 0·635, fractions of which boiled at 80°, 91°, and 102°. At 850°, a high proportion of the liquids boiled between 80—90°, and a further portion at 108°. Butadiene was found in the gases at 750°, 800°, and 850°.

The yield of liquid products reached a maximum at 850°, representing 23·0% of the propane passed. The liquids obtained at temperatures below 800° did not solidify in the cooled receivers (about −80°) and were mainly unsaturated hydrocarbons. Above 800°, they were mainly aromatic.

A study of the gas analyses and volume changes shows that (1) the proportion of hydrogen increased continuously with rise of temperature of decomposition; (2) the proportion of methane reached a maximum at 850° and that of ethylene at 750°. In the products of decomposition at 700°, the proportions of ethylene and methane (corrected value) were nearly equal, indicating that the propane had decomposed in two ways: (*a*) $C_3H_8 = CH_4 + C_2H_4$ and (*b*) $C_3H_8 = H_2 + C_3H_6$, the values showing that, of the propane that decomposed, 60% did so according to (*a*) and 35—39% according to (*b*). This calculation was confirmed by estimating the propylene in the gases by the method of Manning, King, and Sinnatt (*loc. cit.*).

n-*Butane* (see Table IV). At 650°, traces of a low-boiling (−5°) oil were obtained, and bromination of the liquefied gases showed the presence of butadiene. The gases also contained a high proportion of ethane. At 700°, as with propane at 750°, an unsaturated oil, liquid at −80°, was produced. Fractions of this oil boiled at 33°

TABLE IV.

The Decomposition of n-*Butane.*

					Gas analyses, % (by vol.).				
Temp.	Increase in vol., %.	Total liquids, %.	Benzene fraction, %.	C, %.	Higher olefins.	C_2H_2.	C_2H_4.	H_2.	CH_4.*
650°	7·1	—	—	—	24·6	1·4	16·2	8·1	Nil
700	87·5	5·8	2·2	—	19·7	2·4	20·4	10·3	19·9
750	103·6	13·6	8·9	Trace	11·9	3·3	23·6	10·6	40·0
800	140·0	21·1	12·9	,,	3·6	0·7	19·0	23·2	46·2
850	—	24·5	12·7	0·9	2·1	—	15·9	25·2	51·8
900	—	20·9	9·3	6·7	0·7	—	7·9	35·0	54·2
950	215·0	8·7	4·6	19·6	0·2	—	2·0	68·1	29·7

* Minimum values.

and 93°, the bulk distilling below 70°. The gases contained butadiene and much ethane. At 750°, the bulk of the liquids boiled between 80—120°, and the gases contained butadiene and some ethane. At 800°, most of the oils solidified in the cooled condensers; the gases contained butadiene. At 850°, 900°, and 950°, the oils (chiefly benzene) became progressively darker in colour and naphthalene was formed.

The total yield of oils reached a maximum at 850°, corresponding to 24·6% of the butane passed. Most of the oils obtained at 700°, and a high proportion of those at 750°, were unsaturated hydrocarbons, but at higher temperatures benzene was the chief liquid product.

The results indicate that at low temperatures (650—700°) butane decomposes in three ways: (*a*) $C_4H_{10} = C_2H_6 + C_2H_4$, (*b*) $C_4H_{10} = CH_4 + C_3H_6$, and (*c*) $C_4H_{10} = H_2 + C_4H_8$; but the gas analyses give no clear indication as to the proportion in which the butane decomposes according to these three equations, for the proportions of propylene and butylene in the higher olefins are not disclosed by them, whilst the proportions of methane, ethane, and butane in the mixture of paraffins obtained at the lower temperature of decomposition could not be determined by explosion analysis. This information was, however, obtained in another way. The gaseous products of decomposition at 650° were passed through bromine water, and when the resulting bromides (98 g.) were distilled under reduced pressure (16 mm.), 88 g. boiling below 80° were obtained, the solid residue being chiefly butadiene tetrabromide. Part of the liquid fraction was treated with zinc–copper couple in alcohol and the olefins thus regenerated, when analysed by the method of Manning, King, and Sinnatt, showed: Ethylene, 43; propylene, 36; and butylene, 21%. Hence, about 40% of the butane that decomposed did so according to reaction (*a*), 35% according to (*b*), and 20% according to (*c*).

TABLE V.

The Decomposition of n-*Pentane.*

Temp.	Total liquids, %.	Benzene fraction, %.	Gas analyses, % (by vol.). Higher olefins.	C_2H_2.	C_2H_4.	H_2.	CH_4.*
600°	79·2	—	15·6	4·9	17·4	6·2	24·0
700	20·0	9·7	18·1	3·3	22·8	10·6	26·4
750	16·2	7·5	8·0	2·8	24·0	13·0	41·0
800	21·4	11·6	2·9	2·1	22·2	17·2	48·5
850	26·8	11·9	1·4	1·7	17·6	29·0	45·2

* Minimum values.

n-*Pentane* (see Table V). Most of the liquid obtained at 700° boiled between 35·8—36·2° (undecomposed pentane), but a fraction distilled at 58° and was unsaturated. At 750°, decomposition of the pentane appeared to be complete, most of the oils (which solidified in the cooled condensers) distilling between 80—84°. At 800° and 850°, also, the liquid distillates were mainly benzene.

A change in the character of the products of decomposition took place at 750°, liquid aromatic hydrocarbons being then formed in increasing quantity up to 850°. The chief constituent of the gases at all temperatures was methane. The proportion of ethylene reached a maximum at 750° and that of the higher olefins at 700°. The proportion of hydrogen increased continuously with increase of temperature.

TABLE VI.

The Decomposition of n-*Hexane.*

Temp.	Total liquids, %.	Benzene fraction, %.	Gas analyses, % (by vol.). Higher olefins.	C_2H_2.	C_2H_4.	H_2.	CH_4.*
600°	87·7	—	23·5	24·4		6·6	30·1
650	63·3	—	23·1	27·6		6·6	32·9
700	35·6	—	21·8	33·2		7·5	37·2
725	27·3	20·4					
750	30·6	19·7	5·8	28·4		16·1	45·3
800	33·7	19·2	3·3	24·9		19·4	48·6
850	33·8	19·0	1·3	1·8	14·2	27·6	6·4
900	30·1	14·6					
950	10·0						

* Minimum values.

n-*Hexane* (see Table VI). Little of the hexane was decomposed at 600°. The gases contained butadiene. At 650° and 700°, some of the liquid collected was unsaturated, and the gases contained propylene and butylene as well as butadiene. At 750°, the oils obtained were of dark colour and solidified in the cooled condensers, boiling for the most part at 80°.

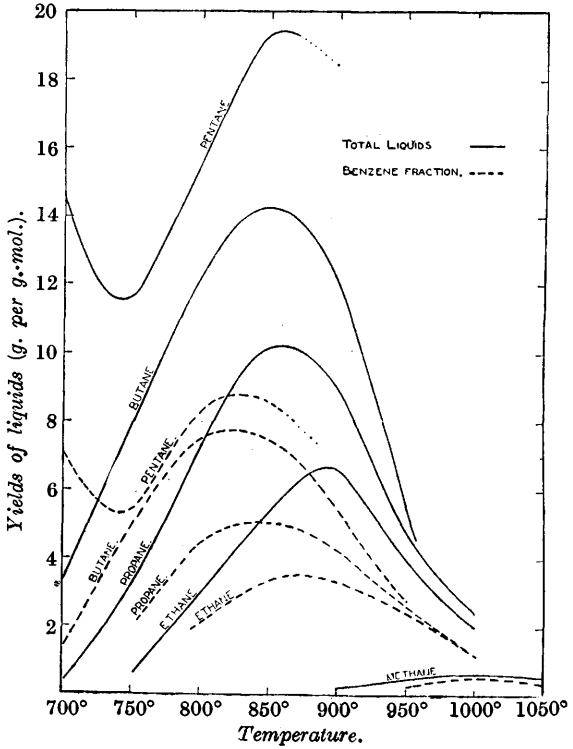
The results were similar to those obtained with *n*-pentane. Decomposition was appreciable at 600° and apparently complete at 725°. Above that temperature, the yield of liquids increased to a maximum at about 850°, 33·8% by weight of the hexane passed being transformed into liquid hydrocarbons (chiefly aromatic) at that temperature. The nature of the gases changed between 700—750°, corresponding with the production of aromatic hydrocarbons. At 600°, a liquid of b. p. 59° was obtained which, as judged from its similarity with liquid fractions obtained during the decomposition of butane and pentane, was 1 : 5-hexadiene. At 650°, the liquids obtained began to boil at 30°, suggesting the presence of C_5 compounds such as the amylene found by Haber (*loc. cit.*). From the gas analyses it would appear that at temperatures up to 700° the important reactions are those of "demethanation" (compare Haber), "de-ethylenation," and "dehydrogenation," in the order named.

Perhaps the most striking feature of the results considered as a whole is the similarity in behaviour of all the hydrocarbons, methane included, at the higher temperatures. Below 750°, when the primary decompositions are taking place, each hydrocarbon follows its own proper course, but at the higher temperatures the (secondary) reactions are similar with all.

The temperature range 700—750° is a transition period. Within that range, with all the paraffins except methane, the production of ethylene reaches a maximum. Under similar conditions, the same types of liquids (aromatic hydrocarbons) are obtained throughout the series from ethane to hexane. The common source of these liquids would therefore seem to be a C_2 unsaturated hydrocarbon. Acetylene has for long been regarded as the source of benzene during decompositions of this character, but recent work, *e.g.*, Davidson's (*loc. cit.*), has stressed the absence of acetylene from the gaseous products. Davidson found, also, that on passing mixtures of acetylene, ethane, and propane through a tube heated at temperatures ranging from 550—950°, acetylene could always be detected in the products even though its original concentration was as low as 0·1%. In the present work, although acetylene has been recorded in the gas analyses, treatment of the gaseous products on a large scale with ammoniacal silver chloride has yielded but traces of precipitate, whilst no acetylene tetrabromide has been obtained on their bromination. Further, on treating acetylene in a similar manner to the paraffins (see later), we have found that the maximum yields of benzene by polymerisation are obtained over the range 650—700°. Aromatic hydrocarbons would be expected from the paraffins over this temperature range were acetylene their source, whereas they are not produced below 750°.

Ethylene alone fulfils all requirements as a producer of benzene in these experiments. It is fairly stable up to 750° and yields aromatic hydrocarbons above 700°. In the decompositions of the paraffins, the yields of ethylene are proportional to the percentage yields (at a higher temperature) of aromatic hydrocarbons. Thus with ethane, propane, butane, and pentane the maximum percentage of ethylene in the products of decomposition is about 24, and the maximum yield of liquid products, expressed as a percentage by weight of the hydrocarbon passed, is about 24 with each. With hexane, the maximum percentage of ethylene is 33·2 and the maximum yield of liquid products is 33·8%.

Fig. 2.



The yields of liquids, and the temperature ranges over which those yields were obtained, are shown graphically in Fig. 2, where the yields, expressed in g. per g.-mol., are plotted against temperatures of decomposition. The results for hexane have been omitted to avoid rendering the diagram cumbersome. As the series is ascended from ethane to pentane, the yields of liquids increase approximately in the ratio 2 : 3 : 4 : 5, showing that the percentages (by weight) of these paraffins thus transformed are about the same. That this should be so can perhaps be deduced from the fact that the composition of the gases produced over the critical temperature-range for the formation of liquids (750—800°) is nearly the same for each of these hydrocarbons. Hexane, which yields an abnormally high proportion of ethylene, yields also abnormally high quantities of liquids.

Comparative experiments were made with ethylene and acetylene, more particularly to determine their temperatures of decomposition and polymerisation and the character of the liquid products yielded by them.

TABLE VII.

The Decomposition of Ethylene.

			Gas analyses, % (by vol.).				
Temp.	Total liquids, %.	Benzene fraction, %.	Higher olefins.	C_2H_2.	C_2H_4.	H_2.	CH_4.*
700°	13·5	6·6	9·2	8·2	55·2	5·9	8·7
750	25·5	13·1	4·4	4·8	40·5	13·1	28·8
800	28·9	10·7	1·4	4·2	16·1	27·9	44·0
850	15·5	7·8	0·4	1·1	6·6	35·6	50·0

* Minimum values.

Ethylene (see Table VII). Of the liquids obtained at 700° and 750° (*d* 0·8), half distilled between 80—86°, a small fraction boiling at 72—76°. The gases contained butylene and butadiene. The liquids obtained at 800° were brown; most distilled between 80—84° and some at 120—130°, leaving a residue of naphthalene.

The optimum temperature for the production of liquids (mainly benzene) was between 750—800°, the total yield at 800° representing 28·9% of the ethylene passed. The dilution of ethylene with hydrogen in certain other stream experiments resulted in decreased yields of benzene and the temperature range for the maximum yield was increased, the mixture giving results similar to those obtained with ethane. This result is consistent with the suggested primary decomposition of ethane. The gas analyses show that ethylene is fairly stable up to 750°, as appears also from the experiments with the paraffins, where the maximum concentrations of ethylene in the products of decomposition were obtained between 700—750°. The figures for acetylene in the gas analyses (Table VII) are too high, for the reason previously stated. On passing the gases from decomposition at 750° and 800° through ammoniacal silver chloride, as they issued from the apparatus, only traces of precipitate were formed.

Several stream experiments were carried out at 600°, 650°, and

675°, and the resultant gases brominated. The bromides were distilled and the residual solid, after recrystallisation from alcohol, proved to be butadiene tetrabromide.

A series of experiments, for which we are indebted to Mr. W. L. Wood, M.Sc.Tech., were made in which samples of ethylene were heated at different temperatures in quartz bulbs during three hours, and the resultant gases analysed. Between 400—700° the ethylene was found to polymerise, yielding butylene, the optimum temperature being 500°. Some of the results are recorded in Table VIII.

TABLE VIII.

The Polymerisation of Ethylene.

	Gas analyses, % (by vol.).				
Temp.	Higher olefins.	C_2H_4.	H_2.	CH_4.	C_2H_6.
400°	3·5	96·5	—	—	—
450	8·0	92·0	—	—	—
500	13·7	76·0	—	—	10·3
550	7·9	55·1	2·9	12·0	22·1
600	6·0	30·0	2·7	25·4	35·1
650	4·2	19·0	11·2	52·7	12·9
700	1·9	16·5	15·4	57·5	8·7
750	0·7	8·2	18·7	67·0	5·4

TABLE IX.

The Polymerisation and Decomposition of Acetylene.

				Gas analyses, % (by vol.).				
Temp.	Total liquids, %.	Benzene fraction, %.	C, %.	Higher olefins.	C_2H_2.	C_2H_4.	H_2.	CH_4.*
600°	30·8	—	—	0·8	53·2	4·2	27·9	8·3
650	61·1	26·4	9·7	1·2	29·5	6·9	34·0	23·0
700	61·1	24·8	16·7	1·2	2·4	10·4	43·8	37·1
750	46·7	18·3	22·1	0·2	0·7	8·8	50·1	37·5

* Minimum values.

Acetylene (see Table IX). At 600°, considerable quantities of soft carbon were produced in the reaction tube and fell from it. This carbon had absorbed the bulk of the oils formed. At other temperatures much soft carbon was formed. The maximum yields of liquids were obtained over the range 650—700°, the amount representing 61·1% of the acetylene passed.

This work has been carried out for the Anglo-Persian Oil Company, to whom our thanks are due for permission to publish the results. We wish also to thank Mr. W. L. Wood, M.Sc.Tech., for assistance in the experiments.

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ADDENDUM.

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According to the mechanism of decomposition outlined in this paper, the degradation of the paraffins proceeds by the reversible elimination of a molecule HX, which may be either a paraffin of smaller molecular weight or hydrogen itself. The residue from this initial decomposition is then an olefin, and the process may be compared with the elimination of an acid or of water from any other addition compound of an olefin. Thus the decompositions represented by the equations

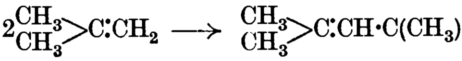
$$CH_3{\cdot}CH_2{\cdot}OH \rightleftharpoons CH_2{:}CH_2 + H{\cdot}OH$$

and

$$CH_3{\cdot}CH_2{\cdot}O{\cdot}SO_2{\cdot}OH \rightleftharpoons CH_2{:}CH_2 + HO{\cdot}SO_2{\cdot}OH$$

may be compared with the pyrogenic decompositions described in the present paper. A more detailed analogy can be found in Butlerow's study (*Annalen*, 1877, **189**, 44) of the equilibrium between *tert.*-amyl alcohol and *iso*amylene in presence of 50% sulphuric acid, $C_5H_{12}O \rightleftharpoons C_5H_{10} + H_2O$. The decomposition of the paraffins is thus pictured as conforming to self-established precedents, and depending on a mechanism of a very general character.

The pyrogenic synthesis is then imagined as proceeding according to two well-established processes, depending on polymerisation and on elimination of hydrogen, successively. The first of these processes, which converts ethylene into butylene, can be compared with Butlerow's conversion of *iso*butylene into *iso*dibutylene :



$$2\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{:}CH_2 \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{:}CH{\cdot}C(CH_3)_3$$

(*Annalen*, 1877, **189**, 65). This process is merely a reversal of the pyrogenic decomposition cited above, since the action can be envisaged most readily as an addition of the radicals $\cdot CH{:}C(CH_3)_2$ and H to the olefin $CH_2{:}C(CH_3)_2$.

The second process converts butylene into butadiene by the elimination of hydrogen, and is identical in type with the original pyrogenic decomposition. It is also analogous to the pyrogenic decomposition of benzene to diphenyl and hydrogen : $2C_6H_6 \longrightarrow C_6H_5{\cdot}C_6H_5 + H_2$. A further application of this mechanism will suffice to convert a mixture of ethylene and butadiene into hexatriene and then into benzene, and the further condensation of benzene with butadiene will give rise to naphthalene, anthracene, and other aromatic hydrocarbons.

A complete survey of the pyrogenic decomposition of the paraffins can thus be made, without the intervention of acetylene, on the basis of a single well-established reaction of the olefins, *viz.*, the reversible addition and subtraction of hydrides of various types, since the polymerisation is merely a special case of reversible addition of a hydride, the olefin itself.

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