CCXXXV.—*The Mechanism of Thermal Decomposition of the Normal Olefins.*

By Richard Vernon Wheeler and William Laurence Wood.

The literature relating to the thermal decomposition of the olefins is scanty. Ethylene alone appears to have received much attention. Day (*J. Amer. Chem. Soc.*, 1886, **8**, 153) found that at 350°, the lowest temperature at which any change took place, this gas yielded polymerides, without the formation of any hydrocarbon with a C/H ratio different from that of the olefins. On raising the temperature to 400°, however, the products were methane, ethane, and liquid hydrocarbons. No carbon was deposited.

Lewes (*Proc. Roy. Soc.*, 1894, **55**, 90; 1895, **57**, 394) considered that at high temperatures, such as 800°, the primary thermal decomposition of ethylene could be represented by: $3C_2H_4 \longrightarrow 2C_2H_2 + 2CH_4$, the acetylene thus formed either polymerising to higher hydrocarbons, such as benzene, or decomposing directly to carbon and hydrogen. Bone and Coward (J., 1908, **93**, 1197) believed the initial effect of a high temperature on ethylene to be an elimination of hydrogen, with a simultaneous loosening or dissolution of the double bond between the carbon atoms, giving rise to transitory residues such as $\vdots$CH. These residues could subsequently combine to form acetylene, or break down to carbon and hydrogen, or be hydrogenated to methane.

Zanetti Suydam, and Offner (*J. Amer. Chem. Soc.*, 1922, **44**, 2036) studied the production of butadiene when ethylene decomposes under the action of heat, and found that its temperature of maximum formation coincided with the appearance of aromatic hydrocarbons. They concluded that butadiene plays an important part in the formation of such hydrocarbons during the pyrolysis of ethylene.

From our own study of the action of heat on ethylene, propylene, and the two non-branched-chain butylenes, we concluded that the principal primary reactions, common to all, involve the formation of either the two-carbon or the four-carbon (or of both) atom members of the olefin series. These primary reactions may be represented by

$$2C_2H_4 \longrightarrow C_4H_8 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (i)$$
$$2C_3H_6 \longrightarrow C_2H_4 + C_4H_8 \quad . \; . \; . \; . \quad (ii)$$
$$C_4H_8 \longrightarrow 2C_2H_4 \quad . \; . \; . \; . \; . \; . \; . \quad (iii)$$

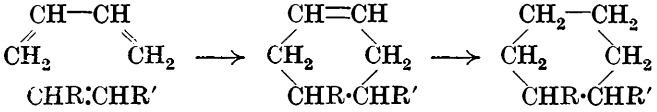
Whilst the exact mechanism of reactions (ii) and (iii) is obscure, it has been found that reaction (i) is a true polymerisation. The butylene is not formed by the condensation of ethylene to butadiene followed by hydrogenation.

Following rapidly on the formation of butylene is a secondary decomposition, its dehydrogenation to butadiene. When butylene is the olefin undergoing decomposition, this change is a primary mode of decomposition. In the presence of hydrogen (liberated during secondary reactions) the olefins decompose through the scission of the carbon chain at the terminal carbon–carbon bond (where such exists), forming radicals which, by hydrogenation, produce methane and the next lower olefin, as represented by

$$CH_3\cdot CH\colon CH_2 \longrightarrow CH_3\cdot + \cdot CH\colon CH_2 \xrightarrow{H\cdot H} CH_4 + CH_2\colon CH_2$$
$$CH_3\cdot CH_2\cdot CH\colon CH_2 \longrightarrow CH_3\cdot + \cdot CH_2\cdot CH\colon CH_2 \xrightarrow{H\cdot H} CH_4 + CH_3\cdot CH\colon CH_2$$

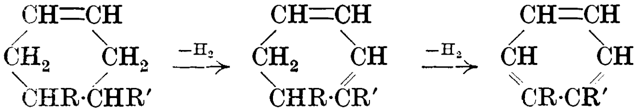
Butadiene and the lower members of the olefin series are always present in the early stages of decomposition. Ethylene and butadiene combine in equimolecular proportion, at comparatively low temperatures, to produce *cyclo*hexene according to the scheme A ($R = R' = H$). Similarly, propylene and butylene combine with butadiene to form substituted hydroaromatic hydrocarbons according to the general scheme A.

(A)



*cyclo*Hexene and methyl*cyclo*hexenes are found in considerable quantity in the liquid hydrocarbons formed from the olefins at the lower temperatures of decomposition. At higher temperatures, the liquids consist essentially of aromatic hydrocarbons, but traces of *cyclo*hexadiene have been detected. *cyclo*Hexene loses hydrogen on being heated, forming benzene, but it is probable that *cyclo*hexadiene is an intermediate product, so that the final stage in the production of benzene from the olefins can be represented by scheme B ($R = R' = H$). Similarly, the final stage in the production of the homologues of benzene can be represented by the general scheme B.

(B)



Analogously to the formation of *cyclo*hexene from butadiene and ethylene, partly hydrogenated naphthalenes could be formed by the combination of butadiene and *cyclo*hexene. These products would then readily be dehydrogenated (compare Jones, J., 1915, **107**, 1582), giving rise to naphthalene, which is found in the liquid decomposition products of the olefins.

EXPERIMENTAL.

The Hydrocarbons.—The olefins were obtained compressed in steel cylinders, the two lowest members of the series being purified by liquefaction and fractionation. The boiling points of Δ^{α}-butylene and of Δ^{β}-butylene were so close together that purification had to be effected by converting them into the dibromides, which were then fractionated, the pure olefin required being regenerated by the action of a zinc–copper couple on an alcoholic solution of the appropriate dibromide.

Butadiene was obtained by regeneration from the solid tetrabromide separated during the estimation of the diolefin in the gaseous products of decomposition of the olefins. *cyclo*Hexene was obtained commercially : it contained traces of benzene.

Method of Experiment.—With each of the gaseous hydrocarbons two types of experiment were made : (1) *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; and (2) *static*, in which the gas, at 400 mm. initial pressure, was enclosed in a quartz bulb of 60 c.c. capacity during different lengths of time at different temperatures, the pressure changes during the decompositions being followed and the resultant gaseous products analysed. Only the "stream" experiments need be described in detail, the results of the "static" experiments being confirmatory.

Stream Experiments.—In carrying out these experiments, the same apparatus and, as far as was appropriate, the same method of procedure were used as for the study of the mechanism of thermal decomposition of the normal paraffins (Hague and Wheeler, J., 1929, 378), which should be consulted for details. The gases were passed into the reaction tube at a constant rate of 4 l. per hour, the duration of heating varying from about 20 secs. at the lower temperatures, when there was a decrease in the volume of the gases, to about 10 secs. at the higher temperatures, when the volume of the gases increased.

The gaseous products of decomposition were subjected to preliminary analysis by the usual methods. For the absorption of acetylene, a 20% solution of mercuric cyanide in 2*N*-sodium hydroxide was used. This solution gave a marked precipitate with prepared mixtures containing 0·2% or more of acetylene, but no such precipitate was detected with any of the gases arising from the thermal decomposition of the olefins. Acetylene, unless in traces only, was therefore assumed to be absent. Further examination of the gases was made by passing them through bromine, to remove unsaturated hydrocarbons, and thence through a tube cooled by solid carbon dioxide dissolved in ether. The absence of condensate in this cooled tube proved the absence from the gases of paraffins of higher carbon content than ethane. The bromides of the unsaturated hydrocarbons were examined by a modification of the method described by Manning, King, and Sinnatt (Fuel Research Board, Tech. Paper No. 19, 1928), in which butadiene tetrabromide was separated from the bromides of the olefins by steam distillation.

The liquids were distilled up to 170°, the distillate being collected separately. With the butylenes in particular, the liquids sometimes contained dissolved gases. These were collected and analysed. They consisted of undecomposed butylene with some butadiene. From each olefin, quantities of liquids sufficient for fractionation and detailed examination were obtained by decomposing 150 litres or more at one temperature.

Carbon deposited within the reaction tube was collected and weighed, though much of it could not be removed by mechanical means. It was always in the form of a glistening foil adhering firmly to the walls of the tube. The reaction tube was thoroughly cleaned by burning it out between successive experiments.

Results of Experiments.—The results obtained with each hydrocarbon are summarised in the tables that follow, the percentages of total liquids, distillate up to 170°, and carbon scraped from the reaction tube being given by weight. The gas analyses are recorded as percentages by volume of the gas entering the reaction tube, not as percentages of the gaseous products of decomposition leaving the tube.

Ethylene (see Table I). At 650°, the principal product was butylene, the percentage by weight of the ethylene passed through the reaction tube that was recovered as gases containing four carbon atoms being 8·4 as compared with 1·5% of liquid hydro-

Table I.

The Decomposition of Ethylene.

Temp.	Total liquids, %.	Distillate up to 170°, %.	C, %.	Change in vol., %.	Gas analyses, % (by vol.).						
					C_4H_6.	C_4H_8.	C_3H_6.	C_2H_4.	H_2.	CH_4.	C_2H_6.
650°	1·5	—	Nil	− 2·7	0·3	3·8	Nil	89·9	0·7	0·5	2·0
700	12·2	8·0	Nil	−15·2	0·4	2·8	2·2	66·2	3·2	4·9	4·9
750	28·2	16·5	Trace	−16·4	0·2	1·5	1·7	47·6	7·2	16·7	8·6
800	36·1	17·7	1·4	−11·8	0·15	Nil	1·1	29·0	17·3	33·7	6·9
850	31·4	13·3	11·9	+ 1·3		0·5		12·2	35·8	49·7	3·3
900	13·4	5·4	13·4	+13·1		Nil		4·6	51·0	55·2	2·2

carbons. At 700°, the production of butylene had decreased but that of butadiene had increased and propylene had made its appearance. That the propylene should be regarded as a secondary product (from butylene formed primarily) was shown by separate experiments, not here described, and can be deduced from the results obtained with the pure butylenes (*q.v.*). Evidence of the disruption of the ethylene molecule, to form molecules of lower carbon content, was first obtained at 750°.

An examination of the liquid products formed at 700° showed that 50% boiled below 110° and was principally benzene, with some toluene and *cyclo*hexene; neither naphthenes nor paraffins were present in this fraction.

Propylene (see Table II). At 650°, the principal products were ethylene, ethane, and butylene, with comparatively small quantities of unsaturated liquid hydrocarbons. Under the conditions of experiment, the formation either of butylene from ethylene or of ethylene from butylene could not occur at this temperature.

Table II.

The Decomposition of Propylene.

Temp.	Total liquids, %.	Distillate up to 170°, %.	C, %.	Change in vol., %.	Gas analyses, % (by vol.).						
					C_4H_6.	C_4H_8.	C_3H_6.	C_2H_4.	H_2.	CH_4.	C_2H_6.
650°	5·2	3·2	Nil	+ 4·0	0·2	4·1	86·9	7·7	0·5	2·1	2·5
700	20·3	12·9	Trace	+10·0	0·6	6·5	45·6	23·5	7·0	18·9	7·9
750	35·6	20·4	Trace	+20·1	0·4	2·0	10·4	37·0	14·4	49·1	6·8
800	40·6	19·0	1·7	+30·1	0·3	0·5	1·5	28·1	23·6	70·7	5·4
850	33·8	14·6	9·5	+46·2		0·5		18·6	36·7	85·9	4·5
900	11·9	6·8	Not determined	+64·2		0·5		8·0	66·5	86·1	3·1

There was a notable difference in character between the liquids of lower boiling point obtained from the decompositions at 650° and at 700°. Whereas the former were mainly monocyclic hydroaromatic hydrocarbons, having one double bond in the ring, the latter were mainly benzene and toluene. At the higher temperature of formation, the proportion of liquids of high boiling point had increased, showing that the more complex hydrocarbons had been formed at the expense of the simpler. The proportion of toluene to benzene formed from propylene at 700° was greater than that formed from ethylene at the same temperature. Naphthenes and paraffins were absent from the liquids boiling below 110°, and were presumably absent also from the liquids of higher boiling point.

TABLE III.

The Decomposition of Δ^{a}-Butylene.

					Gas analyses, % (by vol.).						
Temp.	Total liquids, %.	Distillate up to 170° %.	C, %.	Change in vol., %.	C_4H_6.	C_4H_8.	C_3H_6.	C_2H_4.	H_2.	CH_4.	C_2H_6.
600°	12·9	6·5	Nil	− 23·4	0·9	54·1	7·6	3·2	0·8	8·1	1·9
650	29·8	20·3	Nil	− 10·7	1·7	19·8	24·5	14·2	6·2	37·2	7·1
700	35·8	23·6	Trace	+ 30·0	1·4	2·1	19·6	22·3	11·9	62·1	10·6
750	39·6	22·4	Trace	+ 43·9	0·2	1·3	5·6	31·4	17·3	78·5	9·7
800	39·4	19·9	1·0	+ 57·0	1·0		2·0	30·2	27·2	89·0	7·6
850	35·0	16·2	4·7	+ 73·9	1·0			20·6	50·5	95·7	6·1
900	13·9	7·8	7·1	+104·0	0·9			9·6	85·2	103·3	5·0

TABLE IV.

The Decomposition of Δ^{β}-Butylene.

					Gas analyses, % (by vol.).						
Temp.	Total liquids, %.	Distillate up to 170°. %.	C, %.	Change in vol., %.	C_4H_6.	C_4H_8.	C_3H_6.	C_2H_4.	H_2.	CH_4.	C_2H_6.
600°	5·2	1·4	Nil	− 25·4	0·8	65·0	2·6	1·3	0·9	2·8	1·2
650	27·0	17·2	Nil	− 7·5	1·7	20·0	17·8	8·9	4·9	31·4	7·8
700	37·0	25·8	Trace	+ 27·4	0·9	2·6	19·2	19·8	11·1	62·0	11·8
750	39·6	23·2	Trace	+ 38·9	0·4	2·1	5·3	27·9	17·6	76·5	9·1
800	37·9	18·6	1·4	+52·8	0·5		1·6	24·4	28·4	90·0	7·9
850	31·6	14·2	4·7	+ 68·3	1·2			16·9	48·4	96·1	5·7
900	12·4	6·1	5·4	+100·0	1·6			8·3	83·3	103·1	3·7

Butylenes (see Tables III and IV). Although the Δ^{a}-butylene was the less stable, the products of decomposition from both forms were similar. At 600° and 650° some of the undecomposed butylene was lost through its solution in the liquids. With each form, the production of equal volumes of methane and propylene at 600° indicates rupture of the terminal carbon–carbon bonds, followed by hydrogenation of the radicals so formed. The necessary hydrogen would be liberated during the simultaneous decomposition of some of the butylene to form butadiene. Another simultaneous reaction is the formation of molecules with two carbon atoms, mainly by depolymerisation to ethylene.

Liquid hydrocarbons were produced at 600°, mainly, it is believed, through the combination of butadiene with an olefin. On this assumption, calculation shows that the three primary reactions involved about equal weights of butylene.

An examination of the liquids formed when a mixture of the two butylenes was decomposed at 600° showed that *cyclo*hexene and methyl*cyclo*hexene predominated, benzene and toluene being present in comparatively small proportion. *cyclo*Hexadiene and methyl*cyclo*hexadiene were also present. Only 18·5% of the liquids produced at this temperature boiled above 117°. Of the liquids formed (from Δ^{β}-butylene) at 650°, however, 29·6% boiled above 110° and 16·6% above 150°, and aromatic hydrocarbons now predominated. As with propylene, therefore, an increase in the temperature of formation of the liquids resulted in a greater proportion of higher-boiling hydrocarbons and caused the conversion of hydroaromatic into the more stable aromatic hydrocarbons. Naphthenes and paraffins were absent from the liquids boiling below 110°.

The Combination of Butadiene and Ethylene.—The results of thermal decomposition of the pure olefins, and the observations of earlier workers, suggested that liquid hydrocarbons were formed by the combination of butadiene and ethylene. No experimental proof of this appears to have been adduced hitherto. Proof was therefore sought by heating mixtures of butadiene and ethylene at temperatures at which ethylene by itself was stable. For example, a mixture consisting of 12·85% butadiene and 87·15% ethylene was heated at 600°, and a yield of liquid hydrocarbons of 3·8 g. per 22·4 l. was obtained, the volume of the gaseous products of decomposition being 87% of that of the original mixture.

Increase in vol., %.	Gas analysis, % by vol., on original vol.						
	Butadiene.	C_4H_8.	C_3H_6.	C_2H_4.	H_2.	CH_4.	C_2H_6.
87	1·9	3·1	nil	79·5	1·1	0·8	0·7

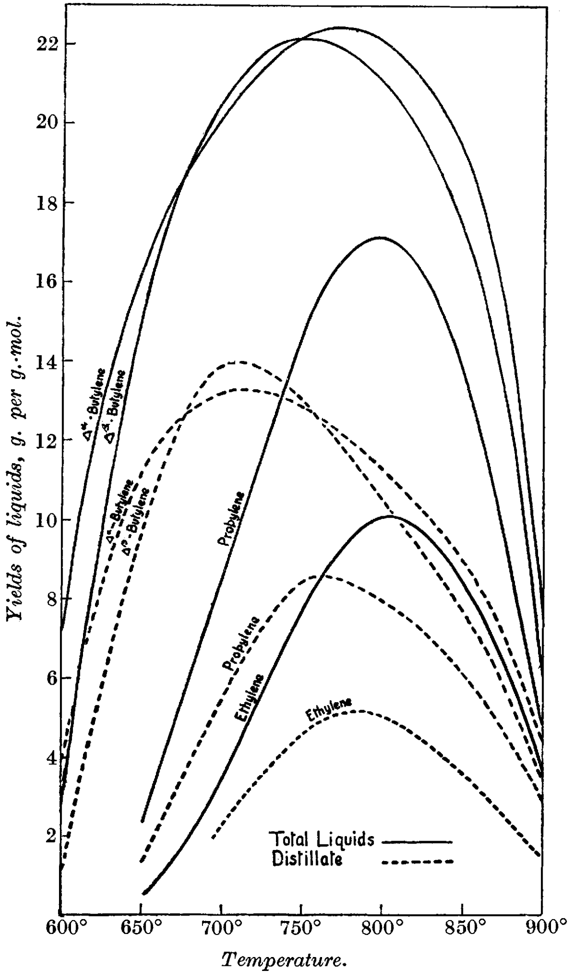
Ethane being regarded as "hydrogenated ethylene," 7 vols. of ethylene had disappeared. Similarly, butylene being regarded as "hydrogenated butadiene," 7·85 vols. of butadiene had disappeared. Only small quantities of gases other than ethylene–ethane and butadiene–butylene were present. The ethylene and butadiene must, therefore, have combined in nearly equimolecular proportion.

On the assumption that the reaction $C_4H_6 + C_2H_4 \longrightarrow C_6H_{10}$ had occurred, an examination of the liquid products was made. The distillate between 75° and 85° (80%) had $d^{20°}$ 0·828 and contained the equivalent of 0·88 double bond in the molecule. The molecular formula, by explosion analysis, was $C_6H_{9.4}$. The bromide had *d* 1·74. These results are all in accord with the distillate being *cyclo*hexene containing a trace of benzene.

The Dehydrogenation of cyclo*Hexene.*—The final step in the suggested chain of reactions by which benzene is formed from the olefins by pyrolysis is the dehydrogenation of *cyclo*hexene. At 550°, this hydrocarbon was barely affected, whereas at 600° appreciable decomposition took place. Its thermal stability, under the conditions of experiment, was therefore about equal to that of butylene.

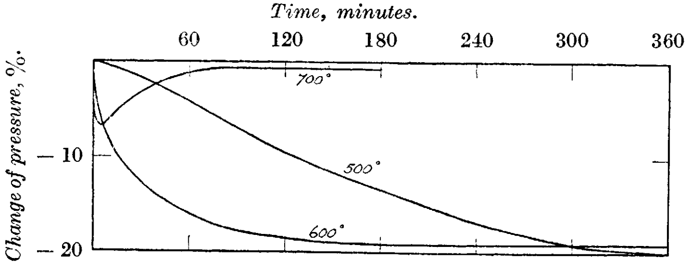
At 600°, 9% by weight of the *cyclo*hexene was converted into benzene, 56% passing through the reaction tube unchanged. At 700°, nearly all the *cyclo*hexene was decomposed, and 25% of benzene (46% of the liquid products) was formed. Evidence was obtained of the occurrence of the reaction suggested by Jones (*loc. cit.*), *viz.*, decomposition to butadiene and ethylene. At higher temperatures of decomposition, the liquids contained a greater proportion of hydrocarbons boiling above 150°, indicating secondary reactions with undecomposed *cyclo*hexene.

FIG. 1.



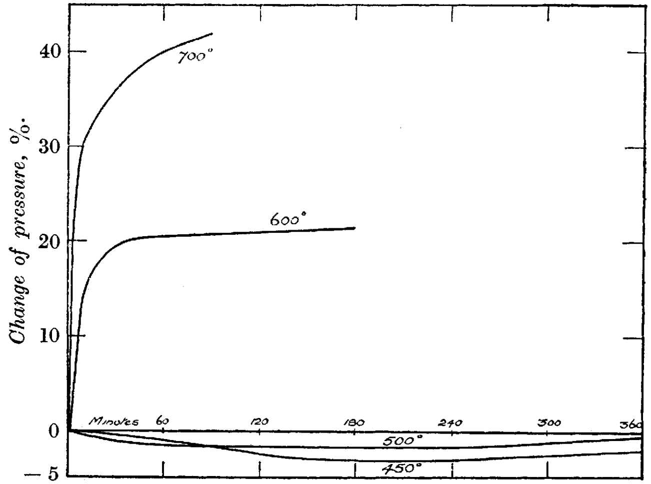
Yields of Liquid Products from the Olefins.—With each olefin, the maximum yield of liquid products, at the optimum temperature, was about 40% by weight. Fig. 1 records the yields of oils and shows that the optimum temperature for their production decreased as the series was ascended. Whereas at the lower temperatures of formation the liquids were mainly unsaturated hydrocarbons, at the optimum temperature the lower-boiling fraction (" distillate ") was mainly aromatic, benzene predominating.

FIG. 2.



Changes of pressure during thermal decomposition (" static ") of ethylene.

FIG. 3.

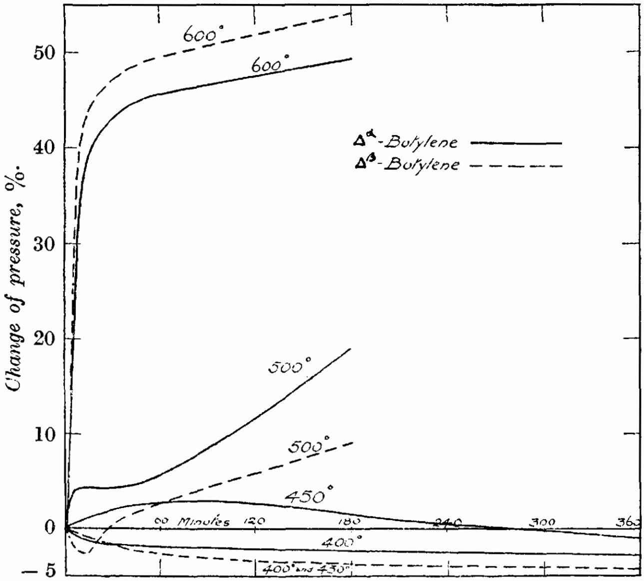


Changes of pressure during thermal decomposition (" static ") of propylene.

Static Experiments.—The minimum temperatures at which decomposition of the gases was observed under the conditions of experiment were: Ethylene, 380—400°; propylene, 350—375°;

Δ^{α}-butylene, 325—350°; Δ^{β}-butylene, 350—375°. Graphs showing the pressure changes during the decompositions are reproduced in Figs. 2, 3, and 4. With the butylenes, the exact course of the pressure changes at the lower temperatures was obscured by the solubility of these gases in the lubricant used on the ground glass joints of the apparatus.

FIG. 4.



Changes of pressure during thermal decomposition ("static") of butylenes.

The Combination of Butadiene and Ethylene.—A series of experiments with a mixture containing 12·5% of butadiene and 87·5% of ethylene at 380° confirmed the result of the " stream " experiments with a similar mixture, *viz.*, that butadiene and ethylene readily combine at temperatures at which ethylene by itself is stable. In each experiment a decrease in pressure was observed equal in amount to the partial pressure of the ethylene that disappeared, the partial pressure of " higher olefins " remaining substantially the same.

This work has been carried out for the Anglo-Persian Oil Company, to whom our thanks are due for permission to publish the results.

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