High-Temperature Pyrolysis of Gaseous Paraffin Hydrocarbons

Methane required, at 1400° C. and 50 mm. pressure, 10 to 20 per cent longer contact time than ethane and propane to obtain maximum yields of acetylene.

Ethane gave at 1100° , 50 mm. pressure, and contact time of 0.0035 second, a maximum yield of 66 liters of ethylene per 100 liters of hydrocarbon charge. At 1400° a similar yield, 67 liters, was obtained with contact time of 0.0004 second. At 1100° the maximum yield of acetylene was 10 liters, while at 1400° 53 liters were obtained. Propylene was formed in quantities of 8 and 5 liters, respectively, at 1100° and 1400° .

Propane gave at 1100° C., 50 mm. pressure and a contact time of 0.008 second, a maximum ethylene yield of 69 liters. At 1400°, 72 liters of ethylene per 100 liters pro-

THE pyrolysis of gaseous paraffin hydrocarbonshas

been investigated from various

viewpoints by many experimenters

(2). At temperatures from 600° to 800° C., ethane, propane, and butanes form olefins, lower paraffins, hydrogen, and liquid hydrocarbons. The factors which favor the formation of liquid hydrocarbons by secondary reactions are pressure and long contact time.

Some experimenters converted gaseous paraffins under temperature conditions at or just slightly above those showing appreciable decomposition so that primary reaction products may be identified. By extrapolating the results to zero decomposition, indications were obtained as to the primary reactions for propane, butane, and isobutane.

The primary products of ethane at a temperature of about 600° are ethylene and hydrogen (8, 11)-a straight dehydrogenation reaction. Propane, subjected to 650° C. showed 51 per cent dehydrogenation, 38 per cent demethanation, and the balance other reaction products (14). With *n*-butane at 600° C., 48.5 per cent demethanation, 34.5 per cent deëthanation, and 16 per cent dehydrogenation were observed (10). Dehydrogenation of 63 per cent, the highest obtained of all the hydrocarbons treated, was produced from isobutane at 600°, while demethanation showed 34.5 per cent (9).

Pyrolysis of methane and ethane has been conducted at temperatures above 1000° C. It was generally believed that the pyrolysis of methane produced primarily carbon and hydrogen, while formation of traces of aromatic hydrocarbons observed by Berthelot (1) was considered as a "side reaction." Fischer and co-workers (4), and later Wheeler (20) were the first to show that by controlling contact time at atmospheric pressure, the formation of gaseous and liquid hydrocarbons having more than one carbon atom is the main reaction, while carbon formation is negligible. At the same contact time and low pressure, liquid hydrocarbon formation is suppressed. De Rudder and Biedermann (13) studied the formation of acetylene from methane at a temperature range of pane charge was the maximum formed at a contact time of 0.005 second. A maximum yield of 15 liters of propylene was obtained at both temperatures. The acetylene formation was 25 liters per 100 liters of propane charge at 1100° , while at 1400° , 76 liters formed at 0.0055 second.

n-Butane yielded at 1100° and contact time of 0.0035 second, 94 liters of ethylene. The maximum acetylene yield was 30 liters and that of propylene 22 liters per 100 liters of *n*-butane charge.

Isobutane yielded at 1100° a maximum of 35 liters of acetylene at 0.004 second. Forty-six liters of propylene was obtained at 0.0035 second. The maximum yield of ethylene was 44 liters per 100 liters of isobutane charge.

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1000° to 1500° C. at subatmospheric pressures. The mechanism of the formation of ethane, ethylene, and acetylene from methane was clearly shown by the work of Storch

(16) and Kassel (6). The pyrolysis of ethane mixed with hydrogen to form acetylene was studied by Fischer and Pichler (3). No experimental work is available on the thermalizing of propane and butane at high temperatures.

The present study covers the pyrolysis of methane, ethane, propane, and butanes at temperatures of 1100° and 1400° C. at 50 mm. pressure and short contact time. The productsacetylene, ethylene, propylene, butenes, and paraffins-from the thermal changes of the hydrocarbons studied are reported with a mechanism of reaction.

Apparatus and Procedure

The pyrolysis of gaseous paraffins was conducted in porcelain (Pythagoras) tubes of 3 mm. inside and 5 mm. outside diameters, except for experiments with propane (at 1100° C.), *n*-butane, and isobutane where quartz tubes of about the same diameter were used. The reaction tube was suspended in the center of a protecting porcelain tube 3.75 cm. in diameter and 65 cm. long, which was heated to 1100° or 1400° C. in a Burrell high-temperature, type B-6 furnace in which the heating unit was made up of four "glowbar" rods. No difficulties were encountered in obtaining the desired temperatures which were measured by means of a platinum-platinum and rhodium thermocouple and potentiometer or millivoltmeter. The thermocouple was placed parallel to the reaction tube, the hot junction being in the center of the porcelain

reaction tube, the not junction being in the center of the porceasin protecting tube. The temperature was constant for 15 cm. length of the reaction tube. The contact time was calculated by dividing the heated volume of the Pythagoras or quartz tube by the average volume of the in- and outgoing gases per second at the temperature and the pres-sure of the experiment. A few critical objections against this calculation may be raised about the actual temperature to which the hydrogeneous ware subjected and the length of the heated the hydrocarbons were subjected and the length of the heated the hydrocarbons were subjected and the length of the heated zone. It was not feasible to measure the temperature inside of the 3 mm.-diameter reaction tube. The temperature of the hydrocarbon gas was therefore determined by the outside wall temperature of the reaction tube. Since turbulent flow of the gases was established, it was concluded that the actual hydrocarbon temperature was close to that of the wall of

TABLE I. PYROLYSIS 50 M	ог Ет Ім. Рг	HANE AT ESSURE	1100°	C. AN	D
Contact time, 10 ⁻³ sec. Ratio, gas out/gas in	$1.53 \\ 1.59$	$2.22 \\ 1.83$	$2.48 \\ 1.86$	$5.85 \\ 2.13$	10.5 2.21
Gas analysis, per cent: C_2H_2 C_3H_4 C_3H_6 O_9 C_0 C_0 C_0	3.4 28.4 4.2 0.4 0.8 0.2	2, 2 32, 2 4, 2 0, 6 0, 4 0, 2	2.2 33.4 2.2 0.6 0.4 0.0	$\begin{array}{c} 4.0\\ 30.6\\ 2.4\\ 1.4\\ 1.0\\ 0.0 \end{array}$	$\begin{array}{c} 4.8\\ 27.4\\ 2.8\\ 1.4\\ 0.8\\ 0.0 \end{array}$
Liters of product/100 l. ethane charge: CeHe C2H4 C3H6	5.4 45.2 6.7	4.0 59.0 7.7	4.1 62.0 4.1	$8.5 \\ 64.5 \\ 5.1$	10.6 60.7 6.2

TABLE II. PYRO	50 Mm	F PRC. PRE	PANE SSURE	AT 11	.00° C). ANI	>	
Contact time, 10 ⁻³ sec. Ratio, gas out/gas in	0.87 1.17	$7 \begin{array}{c} 1.01 \\ 1.26 \end{array}$	$egin{array}{c} 1.25 \ 1.49 \end{array}$	$\begin{array}{c} 2.10\\ 1.96 \end{array}$	$\begin{array}{c} 3.20 \\ 2.09 \end{array}$	$5.13 \\ 2.28$	${11.5\atop 2.39}$	56.4 2.86
Gas analysis, per cent: C_2H_2 C_2H_4 C_8H_6 C_8H_{2n-2} H_2 O_2 CO CO_2 CO_2 N_2 n of paraffins	0.0 8.1 5.2 74.7 7.8 0.3 0.0 0.0 3.9 3.03	$\begin{array}{c} 0.0\\ 12.1\\ 5.8\\ 67.8\\ 11.2\\ 0.0\\ 0.3\\ 0.0\\ 2.8\\ 2.85\end{array}$	$1.3 \\ 18.7 \\ 7.7 \\ 51.9 \\ 17.4 \\ 0.6 \\ 0.2 \\ 0.0 \\ 2.2 \\ 2.47 \\$	1.826.77.631.323.60.61.10.07.32.01	$\begin{array}{r} 4 & 1 \\ 29 & 5 \\ 6 & 2 \\ 30 & 2 \\ 25 & 8 \\ 0 & 4 \\ 0 & 0 \\ 0 & 4 \\ 0 & 0 \\ 3 & 4 \\ 1 & 71 \end{array}$	6.9 29.2 3.8 29.3 28.0 0.6 0.4 0.3 1.5 1.44	$\begin{array}{c} 7.2\\ 28.4\\ 2.4\\ 27.4\\ 31.2\\ 0.4\\ 0.2\\ 1.0\\ 1.8\\ 1.22 \end{array}$	$\begin{array}{c} 8.1 \\ 17.8 \\ 0.0 \\ 24.8 \\ 40.6 \\ 0.9 \\ 1.2 \\ 0.4 \\ 6.2 \\ 1.05 \end{array}$
Liters of product/100 i. propane charge: C ₂ H ₂ C ₃ H ₅ C ₃ H ₅ Carbon formed, per cent of total C in charge	$0.0 \\ 9.5 \\ 6.1 \\ 0.0$	$0.0 \\ 15.2 \\ 7.3 \\ 0.0$	$1.9 \\ 27.9 \\ 11.5 \\ 1.8$	$3.5 \\ 52.3 \\ 14.9 \\ 2.0$	$8.6 \\ 61.8 \\ 13.0 \\ 3.0$	15.8 66.6 8.7 5.0	17.2 68.0 9.1 7.7	$23.2 \\ 51.0 \\ 0.0 \\ 21.5$

TABLE III.PYROLYSIS OF n-BUTANE AT 1100° C. AND50 Mm.Pressure

Contact time, 10 ⁻³ sec. Ratio, gas out/gas in	$\begin{array}{c} 0.921 \\ 1.40 \end{array}$	$1.26 \\ 1.96$	$\begin{array}{c} 2.56 \\ 2.58 \end{array}$	$\begin{smallmatrix} 8.44\\ 2.72 \end{smallmatrix}$	
Gas analysis, per cent: C_2H_4 C_2H_4 C_1H_6 C_1H_{6-2} H_2 O_2 CO CO CO_2 N_2 n of paraffins	$\begin{array}{c} 2.8\\ 17.1\\ 13.2\\ 54.7\\ 11.5\\ 0.5\\ 0.2\\ 0.0\\ 0.0\\ 3.56\end{array}$	2.5 28.4 11.3 38.6 17.4 0.4 0.2 0.0 1.2 2.73	$\begin{array}{c} 6.8\\ 35.8\\ 7.6\\ 24.9\\ 22.7\\ 0.4\\ 0.2\\ 0.0\\ 1.6\\ 1.43\end{array}$	9.533.23.224.727.00.20.40.51.31.26	
Liters of product/100 l. n-butan	e 0.00		1.10	1.20	
$\begin{array}{c} \text{charge:}\\ C_2H_2\\ C_2H_4\\ C_3H_6 \end{array}$	${3.9\atop 24.9\atop 18.6}$	$\begin{array}{r} 4.9 \\ 55.5 \\ 22.2 \end{array}$	$17.5 \\ 92.3 \\ 19.6$	$25.8 \\ 90.3 \\ 8.7$	
Carbon formed, per cent of total C in charge	0.0	1.2	2.5	5.7	
Contact time, 10 ⁻³ sec. Max. yields of ethylene, liters/10 hydrocarbon	01.	Ethane 3.5 66	Pro- pane 8	n-Bu- tane 3,5 94	

the reaction tube. There may be a little uncertainty with regard to the length of the heated zone. Since all the experiments were carried out in the same furnace, the deviation of contact time, calculated from the volume of the zone assumed to be brought to the operating temperature, from the actual would therefore be constant.

The gaseous paraffin to be cracked flowed from a steel storage tank through a pressure regulator and a wet test meter, and was dried in a calcium chloride tower before it passed through a flowmeter into the reaction tube. The gas was then cooled in an iron Liebig condenser and passed through a trap. The pressure was measured by a mercury manometer placed at the condenser exit. The rate of flow and the pressure of 50 mm. were held constant by means of two microscrew clamps, one of which was located at the entrance to the reaction tube, the other after the trap. The reduced pressure and the flow of the gas was maintained by three Nelson pumps in parallel or, when necessary, by a Crowell type D-4 pump, at the outlet of which a wet test meter measured the gas. A sample for analysis was taken before the gas entered the meter.

the meter. Complete analysis of the gas was made by absorption and combustion methods. Acetylene was determined by alkaline potassium iodomercurate solution $(5, \gamma)$, isobutylene with 65 per cent and propylene with 87 per cent sulfuric acid (18), and ethylene with bromine water. Carbon formed was calculated from the carbon-hydrogen balance of the hydrocarbons processed. From the analysis and the volume increase of the reaction gas, the yields of acetylene, ethylene, propylene, and isobutylene were calculated.

Methane and ethane used for the experiments were compressed gases obtained from the Ohio Chemical Company. In order to remove traces of higher paraffin hydrocarbons from methane, the gas was passed through a charcoal absorption tower reported by Storch and Golden (17) to produce

pure methane. The ethane and *n*-butane were pure. The isobutane was a technical product of 98 per cent purity. The propane contained 3 per cent noncondensables.

The results of the experiments are shown in Tables I to VII and plotted in Figures 1 to 7. When the volume yields of the reaction products were plotted in arithmetic scale against the contact time logarithmically, in general the ascending and descending parts of the graphs are straight lines.

Pyrolysis of Ethane, Propane, and *n*-Butane at 1100° C.

The pyrolysis of ethane, propane, and *n*-butane at 1100° with varying contact time proceeded in a similar manner. Ethylene is a primary reaction product from all three hydrocarbons, while acetylene formation is small in the range of

contact times used in the experiments. The acetylene formation increased with increased contact time. Although the

maximum yields of acetylene were not obtained, one can estimate that ethane will not give more than 10 liters of acetylene per 100 liters of ethane at 1100°, even though the contact time is 0.1 second. For propane and n-butane, not more than 25 and 30 liters of acetylene, respectively, were obtained at con-



obtained at contact time of 0.1 second. This conclusion was derived from the data in Tables I, II, and III and Figures 1, 2, and 3.



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The maximum yields of ethylene from ethane, propane, and *n*-butane are as shown in Tables I to III.

The maximum yields of ethylene from ethane and propane were about the same, but *n*-butane yielded moreethylene. The contact times for these optimum ethylene yields were 0.0035, 0.008, and 0.0035 second, respectively. For pro-

pane the time factor was twice as great for the maxium ethylene yield as for ethane and *n*-butane. This may be due to the different character of the reaction-—dehydrogenation in the case of ethane and demethanation in the case of propane. With *n*-butane the cracking into ethane and ethylene may be the primary reaction, and the dehydrogenation of the ethane formed may be a secondary reaction. But with short contact time, it seems more probable that *n*-butane decomposes directly into two molecules of ethylene and one of hydrogen.¹ This decomposition would explain the apparent irregularity of the maximum yield of ethylene from propane at 0.008 second, whereas ethane and *n*-butane yielded maxima at 0.0035 second.



Propylene formed, from ethane, propane, and *n*-butane, with maximum yields of 8, 15, and 22 liters per 100 liters of hydrocarbon treated, respectively, at contact times of 0.001 to 0.002 second, are shown in Tables I, II, and III. In the case of propane and *n*-butane, the formation of propylene

case of propane and can be explained by dehydrogenation and demethanation, but with ethane a union of radicals to form higher hydrocarbons is assumed. It was observed that with propane, *n*-butane, and isobutane, even at the low pressures

¹A mechanism of decomposition of compounds containing a chain of four carbon atoms has been proposed recently by Criegee [Ber., 68, 665 (1935)]. with contact times of 0.008 to 0.010 second or longer. But since no tar formed at short contact time, and maximum propylene yield from ethane resulted with longer contact time, tar formation was probably due to polymerization of acetylene rather than from free radicals.

of the experiment, a small amount of tarry products formed

Pyrolysis of Isobutane at 1100° C.

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The reaction of isobutane takes a different path from that of normal gaseous paraffins under high temperature conditions.

Propylene and acetylene are formed in higher yields from isobutane than from *n*-butane, propane, ethane, or methane.

TABLE IV. I	PYROLYSIS (of Isobur	FANE AT	1100° C.	
Contact time, 10 ⁻³ sec. Ratio, gas out/gas in	1. 1.	$ \begin{array}{ccc} 14 & 2.03 \\ 58 & 2.22 \end{array} $	$\begin{array}{ccc} 3 & 2.50 \\ 2 & 2.42 \end{array}$	$\substack{\textbf{8.85}\\2.71}$	19.8 2.32
Gas analysis, per cent: C_2H_2 C_2H_4 C_3H_6 Iso-C ₄ H ₈	6. 7. 19. 4.	9 10.8 4 11.0 0 18.8 8 0.0	$11.0 \\ 14.6 \\ 16.6 \\ 0.0$	$10.6 \\ 14.0 \\ 10.8 \\ 0.0$	$ \begin{array}{r} 8.8 \\ 11.0 \\ 4.0 \\ 0.0 \end{array} $
Liters of product/100 l. C ₂ H ₂ C ₂ H ₄ C ₃ H ₈ Iso-C ₄ H ₈	isobutane: 10. 11. 30. 7.	9 24.0 7 24.4 0 41.7 6 0.0	26.6 35.4 40.2 0.0	28.7 37.9 29.3 0.0	20.4 25.5 9.3 0.0
TABLE V. PYR	ROLYSIS OF 50 Mm.	Methani Pressur	е ат 140 .е	00° C. AN	םי
Contact time, 10 ⁻³ sec. Ratio, gas out/gas in	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{ccc} 0 & 5.0 \\ 28 & 1.42 \end{array}$	4.6 1.49	${\substack{14.1\\2,02}}$	100^{a} 2.0
Gas analysis, per cent: C_2H_2 C_2H_4 C_3H_6 O_2 CO Liters $C_2H_2/100$ l. CH ₄	1.6 2. 2.2 2. 0.0 0. 0.2 0. 0.6 0. 1.97 3.	$egin{array}{cccc} 8 & 4.6 \ 2 & 2.2 \ 0 & 0.0 \ 2 & 0.4 \ 4 & 0.2 \ 59 & 6.53 \end{array}$	5.0 1.6 0.0 1.6 0.6 7.45	$\begin{array}{c} 6.0 \\ 1.2 \\ 0.0 \\ 2.4 \\ 3.0 \\ 12.12 \end{array}$	11.0 22.0
^a Experiment No. 33 82 mm. pressure.	of de Rudder	and Bieder	mann (13)) at 1400°	C. and

In Table IV the results are given with a Pythagoras tube for subjecting isobutane to 1100° and 50 mm. pressure. Maximum yields were obtained for each unsaturated hydrocarbon reported. These yields in liters per 100 liters of isobutane are given together with their respective contact times in seconds—namely, acetylene, 28.7 liters at 0.00885; ethylene, 37.95 liters at 0.00885; propylene 41.7 liters at 2.22; and isobutylene, 7.58 liters at 0.001145.

Pyrolysis of Methane, Ethane, and Propane at 1400° C.

The pyrolysis of methane, ethane, and propane was investigated at 1400° C., and the results are shown in Tables V, VI, and VII and Figures 5, 6, and 7. The experiments showed the high thermal stability of methane compared to ethane and propane. Methane required ten to twenty times longer

TABLE VI. PYROLYSIS	of E	THAN	E AT	1400°	C. AN	D 50	Мм.	Press	SURE
Contact time, 10 ⁻³ sec. Ratio, gas out/gas in	$\substack{0.28\\1.72}$	$0.33 \\ 1.73$	$\begin{smallmatrix}0.41\\2.05\end{smallmatrix}$	$\begin{array}{c} 0.56 \\ 2.14 \end{array}$	$\begin{array}{c} 0.88 \\ 2.27 \end{array}$	$\substack{1.61\\2.61}$	$1.64 \\ 2.70$	$\begin{array}{c} 3.04 \\ 2.86 \end{array}$	$9.50 \\ 3.10$
Gas analysis, per cent: C_2H_2 C_2H_4 C_3H_5 C_nH_{2n+2} H_2 O_2 CO N_2	3.2 30.2 2.2 25.8 34.6 0.6 2.8	3.0 31.6 2.8 0.4 0.2 	$\begin{array}{r} 4.8\\32.8\\1.4\\13.4\\41.2\\0.4\\0.6\\5.4\end{array}$	$7.8 \\ 28.2 \\ 1.0 \\ 13.2 \\ 46.8 \\ 0.6 \\ 0.6 \\ 1.4 \\ 0.6 \\ 1.4 \\ 0.6 \\ 0.6 \\ 1.4 \\ 0.6 \\ 0$	12.020.60.612.25.160.40.62.0	$ \begin{array}{c} 13.8\\ 11.2\\ 0.0\\ \\ \\ 0.8\\ 0.8\\ \\ \\ \end{array} $	$ \begin{array}{c} 13.6 \\ 10.6 \\ 0.0 \\ \\ 0.4 \\ 1.0 \\ \\ \end{array} $	17.8 5.0 0.0 0.6 0.0 	$15.4 \\ 0.4 \\ 0.0 \\ 4.9 \\ 70.7 \\ 1.4 \\ 0.6 \\ 6.6 \\ 0.$
Liters of product/100 l. ethan	э., Э	••	1.3	1.0	1.1	••	••	••	1.0
C_2H_2 C_2H_4 C_3H_6 Carbon formed, per cent of	$5.5 \\ 52.0 \\ 3.8 \\ 0$	$\substack{5.2\\54.6\\4.8}$	$\substack{\textbf{9.8}\\\textbf{67.3}\\2.9}$	$16.7 \\ 60.6 \\ 2.1$	$27.3 \\ 46.8 \\ 1.4$	$36.0 \\ 29.3 \\ 0.0$	$\substack{\substack{36.7\\28.6\\0.0}}$	$\begin{array}{c} 50.9\\14.3\\0.0\end{array}$	$47.8 \\ 1.2 \\ 0.0$
total C in charge	0.0	••	0.3	4.7	8.0	••	••	••	44.0

contact than ethane and propane to obtain maximum acetylene yields. A maximum of 12 liters of acetvlene per 100 liters of methane was obtained. De Rudder and Biedermann (13) report yields of 22 liters of acetylene which they obtained at a longer heating time. If no correction is made for de Rudder and Biedermann's

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TABLE VII. PYROLYSIS OF P	ROPAN	E AT	1400°	С. А	.ND 50) Мм.	PRE	SSURE
Contact time, 10 ⁻³ sec. Ratio, gas out/gas in	$\begin{array}{c} 0.39 \\ 2.27 \end{array}$	$egin{array}{c} 0.55 \ 2.59 \end{array}$	$0.85 \\ 2.84$	$\begin{array}{c} 1.29 \\ 3.09 \end{array}$	$1.83 \\ 3.30$	$2.67 \\ 3.39$	$3.40 \\ 3.46$	$5.23 \\ 3.67$
Gas analysis, per cent: C ₂ H ₂	7.0	94	12.6	16 4	17 4	18 4	20.2	20.6
Č2H4 C2H4	28.2	27.0	20.2	13 4	10.4	6.8	3.2	1.8
CnHin+2	27.8	24.6	22.4		•••		15.8	11.8
	0.6	0.4	0.6	0.4	0.4	0.2	0.6	0.0
N_2	2.4	1.8	2.8	0.4	0.4	0.4	2.0	$1.6 \\ 2.0 \\ 1.0 $
Liters of product/100 l. of propane	1,*	1.1	1.0	••	••	••	1.0	1.0
C_2H_2	15.9	24.4	35.8	50.8	57.5	62.4	70.0	75.7
C_2H_4 C_3H_8	64.0 14.5	$70.0 \\ 6.2$	57.5 3,4	$\frac{41.5}{0.0}$	$ \begin{array}{r} 34.4 \\ 0.0 \end{array} $	$23.1 \\ 0.0$	11.1 0.0	$\frac{5.6}{0.0}$
Carbon formed, per cent of total C in charge	2.3	7.1	11.9				26.4	28.1

contact time, as has been suggested by Storch (15), a plot of their results on Figure 5 of this paper will fall on the straight line.

Methane produced small amounts of ethylene, the highest being 3.1 liters per 100 liters at a contact time of 0.005 second. Some ethane, but no propylene, was detected among the re-



action products. The formation of ethane and of ethylene can be expected since Storch (16) has shown that ethane is the first product which was isolated in the pyrolysis of methane; 95 per cent conversion of the reacted methane to ethane was obtained in experiments at low pressures in a carbon filament lamp immersed in liquid nitrogen.

The pyrolysis of ethane and propane proceeded similarly at 1400° C. to that of 1100°. At contact times of 0.0004 to 0.0005 second, the formation of ethylene reached a maximum. With increasing contact time, ethylene gradually disappeared, while acetylene formation increased. The maximum yields of ethylene, propylene, and acetylene are as follows:

	Ethylene	Propyl- ene	Acety- lene
From ethane: Liters/100 l. hydrocarbons processed 10 ⁻³ sec.	$\begin{smallmatrix} 67 \\ 0.4 \end{smallmatrix}$	5 0.33	$53 \\ 5.5$
From propane: Liters/100 l. hydrocarbons processed 10 ⁻³ sec.	$72 \\ 0.5$	$\substack{14.5\\0.39}$	$\begin{array}{c} 76 \\ 5.5 \end{array}$

It is interesting to note that the contact times for the optimum formation of ethylene, propylene, and acetylene were the same in the case of ethane and propane.

The maximum yields of ethylene from both paraffin hydrocarbons were about the same at 1400° and 1100° C., but the contact time at the higher temperature averaged about oneeighth that of the lower temperature.

Much higher yields of acetylene, 53 and 76 liters per 100 liters of ethane and propane, respectively, were obtained at 1400° as compared to 1100° C.

Carbon Formation

With increasing contact time, carbon was formed in the pyrolysis of gaseous paraffin hydrocarbons at 1100° and 1400° C. At 1100° the carbon formation was zero at 0.001 second and gradually increased to 6 to 8 per cent of the total carbon content of the hydrocarbon charged when the time was 0.01 second. The increase in the carbon formation is directly proportional to the logarithmic increase in contact time. The carbon formed is a hard shiny film.

General Consideration

The thermal decomposition of hydrocarbons by high temperatures consists in a series of consecutive reactions which are of primary,

secondary, tertiary, etc., nature. The primary products are in no way connected with real equilibrium. We may call such a reaction a "transition" one. This type of reaction is defined by temperature, pressure, and contact time. Any catalytic influence due to the walls of the reaction tube

may be omitted from this discussion. The three physical factors determine the products which are obtained. The primary products are not stable under the conditions of the reaction, decomposing to secondary, tertiary, etc., compounds. The final products of every pyrolysis of hydrocarbons tend toward carbon and hydrogen. Only small quantities of simple hydrocarbons, such as methane, ethylene, and acetylene, can exist in the system of hydrogen and carbon in the temperature range 1200° to 2000° C. at sub- or atmospheric pressure when true equilibrium is established.

The amount of methane which is in equilibrium with hydrogen and graphite at atmospheric pressure and 1200° C. is 0.24 and 0.07 per cent at 1500° C. (12). At 1800° C., 0.13 per cent acetylene is in equilibrium with carbon and hydrogen (19).

The most decisive factor in a transition reaction is



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the contact time which determines the composition of the reaction products. In the range of 1100° and 1400° C., temperature was without material influence on the yield of primary products. This was shown with the ethane and propane which yielded the same maximum percentages of ethylene at both temperatures. Temperature had a greater influence on the yield of secondary products than of the primary. Ethane and propane produced small yields of acetylene at 1100° C. In the case of propane at 1400° C. the maximum acetylene yield was higher than that of ethylene. Ethane formed about seven times more acetylene at 1400° than at 1100° C.

Acknowledgment

The writers appreciate the assistance given by H. T. Bollman and C. I. Parrish in this work.

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RECEIVED May 8, 1935.

Catalytic Polymerization of Gaseous Olefins by Liquid Phosphoric Acid

I. Propylene

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HE polymerization reactions of the olefins X have been less studied from a theoretical point of view than their other reactions, such as halogenation. During recent years interest in the gaseous olefins has grown apace because of the enormous quantities produced as a by-product of the cracking industry.

Liquid phosphoric acid is an effective catalyst for the polymerization of propylene. An explanation of its catalytic action is based on its ability to form esters with olefins. The ester molecules are assumed to react with each other to produce polymer and regenerate phosphoric acid or to liberate activated olefin molecules which react with molecules of ester or other molecules of olefin to produce polymers and regenerate phosphoric acid.

Experiments have shown that olefins react with phosphoric acid at relatively low temperatures (200° C. for ethylene, 125° C. for propylene) to form esters:



These esters have been isolated and subsequently converted into polymer and phosphoric acid; that is, the polymerization process has actually been carried out in two steps as postulated by the hypothesis.

At the temperatures employed in polymerization, the life of these esters is probably very short. A single molecule of phosphoric acid should be able to bring about the polymeri-

Propylene polymerizes in the presence of liquid phosphoric acid to a mixture of monoölefins. Propylene polymerizes more readily in the presence of the more reactive butylenes than when alone. A mechanism has been suggested for the polymerization of olefins in the presence of phosphoric acid which involves the formation of intermediate esters.

zation of many molecules of olefin since the acid is regenerated after each cycle. In one experiment on the polymerization of propylene, the quantity of polymer obtained corresponded to the polymerization of 110 molecules of propylene by a single molecule of phosphoric acid, and at the end of the experiment the acid was as active as it was at the beginning.

The following equation represents the decomposition of 2 molecules of isopropyl phosphoric acid with the regeneration of 2 molecules of phosphoric acid and the formation of hexylene:



The esters may eliminate the elements of phosphoric acid in different ways, thus giving rise to isomeric polymers. The first formed, hexylene, may react with phosphoric acid to form hexyl phosphoric acid which in turn may react with

propyl phosphoric acid to produce nonylene. In the same way nonyl phosphoric acid may react with propyl phosphoric acid to form dodecylene, or 2 molecules of hexyl phosphoric acid may produce dodecylene.

Under moderate polymerizing conditions, 135° to 200° C. at 1 to 15 atmospheres pressure, propylene polymerizes to a liquid consisting almost entirely of monoölefins, presumably