Hydrocarbons from Carbide (A) II.* Non-Catalytic Polymerization under Ordinary Pressure. Hydrogen Systems and General Experimental Details.

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The acetylene molecule owes its unique reactivity to the unsaturated triple bond and high negative heat of formation. The unsaturated property enables it to polymerize readily into simple or complex molecules. When the nascent acetylene molecule is formed from calcium carbide by the action of water, it probably possesses more energy and reactivity than ordinary acetylene and it is even more capable of further polymerization. This extra reactivity would manifest itself in the lowering of the polymerization temperature, independent of its main reaction from the influence of environments, and it has actually increased the yield of products as compared with the results of ordinary acetylene reactions.

With the purpose of obtaining a maximum yield of liquid hydrocarbons, utilizing this excess reactivity of nascent acetylene, we have attemped the present series of investigations. In order to make the effect as evident as possible, we have tried non-catalytic experiments under the ordinary pressure. In our present discussion we shall neglect any catalytic effect(1) of such products of the reaction as calcium oxide, carbonate, and carbon. In fact, we have found their effects—if any—rather small. This point will be taken up again later.

In this paper, first, general methods of experimental procedure and analyses of the products are given sufficiently minutely in order to offer some information with regard to the probable sources of difficulty and errors and to the degree of accuracy of the results to be expected not only in this report but also in the whole series of investigations. Second, these experiments with hydrogen (and nitrogen) have been carried out somewhat in detail to determine the optimun conditions for liquid synthesis which will serve as a basis for the ensuing investigations with carbon dioxide, acetylene, and water gas.

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* Hydrocarbons from Carbide, Thermodynamics by R. Negishi, O. Kimura, and O. Kamiike, *Rev. Phys. Chem., Japan,* **15** (1941), 31 will be henceforth referred to as Paper (A) I. (A) will be used in contradistinction to Papers from I to VI on the same subject which have been published in Japanese in *J. Soc. Chem. Ind., Japan,* (1941–1942). In those papers experimental details have been minutely given. In the present series of papers, which will appear in this Bulletin, most of the experimental details will be abridged, and only a minimum of them, pertinent to the discussion of the results, will be included.

(1) G. Egloff, Reactions of Pure Hydrocarbons, Reinhold Publish. Corp., N. Y. (1937); C. Ellis, The Chemistry of Petroleum Derivatives, Reinhold Publish. Corp., N. Y., Vols. I and II (1934 and 1937).

Experimental Details. (1) Materials. Carbide. A commercial product which had the following composition* was used:

Component	% by Weight
Acetylene	85–75
CaO	12–19
$CaCO_3$	0.8–1.8
SiO_2	1.7–2.5
CaS	0.3–1.2
Ca_3P_2	0.2–0.5

Hydrogen. Commercial electrolytic hydrogen of which purity was rather inferior (about 97%, the rest being air) was used without any purification.

Nitrogen. A commercial product compressed in a cylinder was used without any purification.

The other gases used in the later investigations will also be given here.

Carbon Dioxide. A commercial product of about 99.5% purity was used without any purification.

Carbon Monoxide. It was prepared by the action of formic acid on hot concentrated sulphuric acid. It was partially purified by bubbling through a KOH solution (20%) and distilled water.

Acetylene. It was prepared by dropping the carbide grains of 1 to 2 mm size into excess of water. The gas was bubbled through several wash bottles containing distilled water. No further treatment was effected.

(2) *Apparatus.* The reaction gas was first collected into two 20-liter bottles so arranged that while one was being discharged, the other could be filled up simultaneously. By this means an uninterrupted flow of gas was possible. The gas was passed through a gas meter and then a water reservoir, or a saturator, maintained at a constant temperature (within ±0.1°C) by means of a well insulated automatic regulated thermostat. The temperature of the bath, consequently that of the water in the saturator was so adjusted as to give a proper water vapor-gas ratio. The vapor and gas and their mixtures were assumed ideal in calculating their compositions. The saturated gas was passed from the top to the bottom through the carbide layers, sandwiched between those of glass wool, occupying about 50 cm. of a Terex glass reaction tube of 2.5–3 cm. diameter. By inserting the layers of glass wool, cracking and breaking of the reaction tube due to packing effect, caused by $CaCO_3$ formation, were prevented to some extent. Usually, 200 g. of the carbide grains per run was used. The reaction tube was heated by means of an automatically regulated electric furnace of 75 cm. length. The temperature could be easily maintained within ±2°C and most of the time within ±1°C. The products were condensed, first, by a water-condenser and then by a trap cooled with a mixture of solid CO_2 and alcohol. The condensates in the condenser were designated as "condenser" and those in the trap "trap." The non-condensable gas was passed through a second gas meter and collected in a second set of two 20-liter bottles similarly arranged as the first. When one of the bottles was filled up, a gas sample was taken for analysis. Usually, a complete run required from 8 to 10

* The authors are grateful to Messrs. Kataoka, Kodama, Nakano, and Inaba for this as well as for most of the liquid and solid analyses given in this series of investigations; also to Messrs. Nagayoshi, Shimamura, and Maruyama for performing the experiments.

hours. The whole apparatus was made of Terex (similar to Pyrex) glass. Only where metal was connected to glass, rubber tubing was employed. The oil vapors never seriously came in contact with rubber at any point. The apparatus was equipped with by-pass from which nitrogen could be introduced to flush out the air in the reaction tube. A thermocouple was inserted from the bottom. It was so long as the temperatures at various points in the carbide reaction zone could be observed.

(3) *Methods of Analysis.* Since the detailed description of the methods of analysis used has been given in one of our papers[2] it will not be repeated; however, as has been mentioned above, a minimum of it, indispensable to a fuller appreciation of the results discussed here and in the subsequent papers, will be given.

Carbide. Acetylene and carbonate contents were determined from the volumes of the gases developed by treating it with a 25% NaCl solution saturated with acetylene and with the above solution acidified with phosphoric acid, respectively. The gases were collected over the same solution. The total carbide analysis was made by alkali fusion, and Si, S and P were determined, respectively, as SiO_2, SO_4, and PO_4.

Solid Residue. Any free, or decomposed, carbon and high polymers in the residue were determined together by elementary analysis after the carbonate and acetylene had been eliminated by the above method. The residue was extracted with chloroform when necessary.

Gas. Since our investigations were exploratory in nature, a large number of samples, containing complex mixtures of such components as CO_2, C_2H_2, olefins, O_2. CO, H_2, saturated gases, and nitrogen, had to be analysed. We finally adopted as the most suitable method for our purpose, both in speed and accuracy, a modified method of Schuftan, which in turn was a modification of Orsat's. Speed was gained at the expense of accuracy; accuracy of 5% must be considered satisfactory.

All of the gases, except hydrogen and the saturated ones, were determined by absorption with usual reagents. Hydrogen was determined by catalytic and selective combustion with copper oxide at 200–300°C; the saturated gases, by explosion. One of the most troublesome features and, at the same time, the source of the greatest uncertainty in our method was the absorption of acetylene in the CO_2 absorption medium. This was finally overcome by saturating the KOH solution with Na_2SO_4, and passing the sample through the medium just once which was sufficient to absorb all of CO_2 and but slightly of acetylene. The results of Table 1 are instructive in this connection.

Liquid Products. The liquid products were subjected to elementary analysis, and usually the oxygen content was calculated by difference; however, direct oxygen determinations were made if necessary. In most of the cases calculation by difference was sufficient for our purpose. Combined products from different runs were subjected to distillation, and the various fractions were determined from their boiling ranges and other physical constants. The liquid products of these runs contained small amounts of sulphur, nitrogen, and oxygen as phenols and

(2) O. Kamiike, S. Kataoka, M. Nibayashi, and R. Negishi, Paper II.

Table 1. Solubility of Acetylene in KOH Solution. (Purity of acetylene, 95.2).

No. of pass through absorb. medium	% C_2H_2 Absorbed		
	KOH (1 : 2)	KOH (1 : 2) Sat'd. with NaCl	KOH (1 : 2) Sat'd. with Na_2SO_3
1	9.0	3.9	1.0
2	16.4	6.7	5.6
3	22.6	13.0	8.0
4	29.1	16.2	11.9
5	34.7	19.0	13.1
10	60.3	33.2	26.1

* If a sample contains less acetylene, the percentage absorbed will be less.

ethers. Alcoholic products, however, constituted the major portion of the oxygenated compounds in the product.

Results and Discussion. Since the experimental data on the formation of hydrocarbons directly from carbide[3][4][5] is scarce, the authors have undertaken to conduct some experiments to find out the optimum conditions for the best yield of liquid products. Hydrogen (and nitrogen) saturated with the water vapour at about 80°C* has been first tried, and the results obtained are given in Table 2 for which some additional explanation may be necessary. In this paper (and also in this series of investigations), the time of contact has been calculated as follows:—the free space in c.c. of the carbide, taken equal to 1/2 of the total weight of the carbide charged, plus the glass wool space is multiplied by the total time in second and the product is divided by the total volume in c.c. at the reaction temperature of the hydrogen (or the reaction gas) introduced. The sum of the percentages in the Table is not necessarily equal to the figures given in the total carbon balance, since part of the carbide has been transformed into C_2H_6 and other products, and none of them has been included in the Table. The deviations of the total carbon and weight balances from 100 serve as a measure of reliability of the results found in the Table.

Effect of Temperature. In Fig. 1 the percentages of the products given in Table 2 are plotted against reaction temperatures. The various points at 300°C are less reliable than those at the other temperatures,

(3) G. L. Putman and K. F. Kobe, *Chem. Rev.*, **20** (1937) 131. This paper contains also other reactions than calcium carbide.

(4) H. Plauson and G. Tischenko, G. P. 346065 (1921); N. V. de Bataasche Petroleum Maatschappij. Holl. P. 22573 (1927); *Chem. Zentr.* 1931, I, 1356; F. Hansgirg, J. P. 127812, 134273, 134712.

(5) S. P. Gambarjan and L. S. Kasarjan, R. P. 41516; A. T. Babayan, *J. Gen. Chem.* (U.S.S.R.) **8** (1938) 602; *Chem. Abst.*, **33** (1939), 1269. In these references the carbide is reacted with acetone and ether to produce some hydroxy-yne compounds.

* At this temperature the ratio of the water vapor to gas is approximately 1 to 0.85. This proportion has been found to give nearly the best yield under our conditions.

Table 2. Hydrogen Systems.

Exp. No.	I_L29	I_L30*	I_L34	I_L35*	I_L31	I_L21	I_L18**	I_L16	I_L25	I_L27
Reaction Temp°C	300		340		380		420		460	
Time of Contact (sec.)...	12.3	14.1	18.1	18.5	12.6	7.8	10.9	10.6	7.3	5.4
Carbide Introd. (g.)	200	200	200	200	200	100	100	100	100	100
Liq.*** Carbon on React. Carbide Carbon (%) ..	15.5	16.0	21.8	13.5	18.4	20.6	11.4	15.3	9.4	10.4
CH_4 (%)	2.1	0.0	3.5	7.3	10.4	5.4	11.8	6.8	9.3	9.7
CnH_{2n} (%)	1.5	0.8	0.6	3.2	4.7	2.1	5.6	4.6	4.5	4.6
C_2H_2 (%)	20.5	24.8	26.7	34.3	23.8	26.8	7.4	19.8	12.6	13.2
(CO_2+CO) %	2.0	2.9	2.5	0.8	3.5	1.3	0.8	0.5	0.6	1.1
Decomp.+High Polym. (%)	11.8	7.3	20.7	48.9	26.8	26.7	49.8	23.8	39.4	44.8
Carbonate (%)	9.5	0.0	3.7	12.3	6.8	9.3	—	12.6	12.0	12.9
Total Carbon Balance ...	78.5	77.8	81.6	102.0	96.8	94.3	93.5	90.6	89.8	96.6
Total Weight Balance ...	99.4	96.0	99.8	100.6	99.8	100.2	98.3	98.1	99.8	99.2

* Nitrogen used. Data not plotted in Fig. 1.
** Data not used in Fig. 1.
*** % of produced carbon on reacted carbide carbon.

but in the general picture of the mechanism of the reactions, they seem to fit sufficiently to warrant their appearance in the Figure. For the sake of convenience, the formations of the products will be discussed in their order of appearance on the 300°C line.

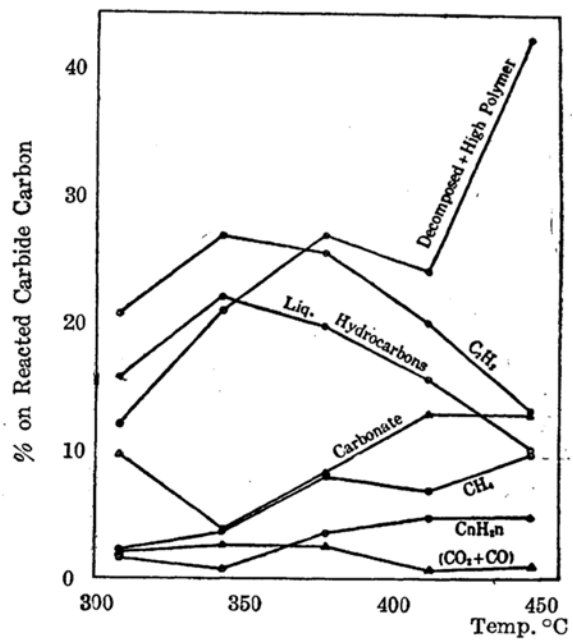

Fig. 1. Effects on Products of Carbide of Temperature.

The amount of free acetylene increases from 300 to 340°C, where it attains a maximum, and then decreases rapidly. There is no satisfactory explanation for this behavior, but from a considerably body of experimental data available from our runs, we may offer some suggestions. At lower temperatures (as at 250°C), we have obtained practically no liquid products, but a large amount of "yellow powder," or cuprene-like substance, and the efficiency of its formation at the temperature is much greater than that of the liquid products at 340°C where the formation of the latter is the

highest. The one run made with hydrogen showed a conversion into the solid product of over 30%* as compared with 21.8% for the liquid. We might assume, therefore, that at lower temperatures the nascent acetylene molecules are in more favorable conditions as regards the effects of thermal agitation and cracking** and of the free energy of reaction[6] for the solid polymerization. As the temperature is raised the sojourn of the acetylene molecules in the favorable positions becomes shorter, and an increased amount of free acetylene is resulted; at still higher temperatures the effects of thermal cracking become striking, and the concentration of it again decreases.

The yield of liquid products must also have a maximum. According to our thermodynamic considerations[6], at lower temperatures the formation of solid polymers predominates, and, as the temperature is raised, the size of the polymers becomes less, and more liquid products are formed. With a further increase of temperature, the size of the molecules decreases further, and the amount of gaseous products increases at the expense of those of the liquid.

The residue is yellow at 250°C and becomes darker with the increase of temperature; at above 400°C it is black. At lower temperatures it may not contain any free carbon, but above 400°C some of it (or polymers with their hydrogens stripped off) is actually present.

The carbonate formation increases with the increase of temperature and is also dependent on the increasing formation of CO_2 with temperature. This CO_2 reacts with the freshly produced CaO from the carbide to form $CaCO_3$.

The sources of CO_2 and CO are not clear. We hesitate to make a definite statement on this point; however, it seems that the formation of CO_2 is intimately associated with CO. Some of the reactions, involving the substances found in the present systems, which may produce CO are given below:

Reaction	ΔF at 400°C
$C + \frac{1}{2}O_2 = CO$	− 40400
$C + CO_3 = 2CO$[7]	+ 12800
$C + H_2O = CO + H_2$	+ 9500
$CH_4 + CO_2 = 2CO + 2H_2$	+ 17200
$CH_4 + \frac{1}{2}O_2 = CO + 2H_2$	− 36000
$CH_4 + H_2O = CO + 3H_2$	+ 13900
$CH_3OH = CO + 2H_2$	− 7400
$CO_2 + H_2 = H_2O + CO$	+ 3300

* With other gases like CO, CO_2, C_2H_2, the % conversion is from 35 to 65% of the reacted carbide carbon.

** At lower temperatures this effect is most pronounced. Since the reactions involving the carbide are highly exothermic, if the rate of reaction becomes sufficiently rapid, the accumulation of the heat of reaction far exceeds the dissipation of the same, and there may set in thermal decomposition and other complications.

(6) Paper (A) I.

(7) A. Semechkova and D. Frank-Kamenetzky, *Acta Physicochim.*, (U.R.S.S.) **12** (1940) 879. According to the investigators, the reaction is $C+CO_2=CO+(CO)$, where (CO) is the adsorbed carbon monoxide, and this reaction takes place at 600°C.

In these reactions the source of oxygen may be that present in the original hydrogen, and CH_3OH has been identified as one of the products. These reactions may require much higher temperatures so that their rates become appreciable than the temperature range in our experiments. The fact, however, that (a) the actual temperature at the point of reaction is higher than that indicated*, (b) most of the reacting partners are in their nascent states, and (c) the products of reaction are removed continuously[8] may induce some of these reactions to proceed as indicated above. Moreover, some of them may take place on the surface of the solid. In this connection the work of Kawakita[9] on the decomposition of CO_2 into C and CO on reduced iron at temperatures as low as 300 to 400°C is suggestive.

The increase in the content of methane with the increase of temperature is as expected from thermodynamic considerations and is borne out by abundant experimental data.

The increase in the formation of CnH_2n with the increase of temperature may be due to partial cracking of the large molecules, on the one hand, and hydrogenation[10] and polymerization[10][11][12] of the acetylene molecules, on the other.

Effect of Time of Contact. Next, we shall consider briefly the effects of time of contact. Although the results are not complete, some information may be gathered from the relationship between the time of contact and the yield of liquid products for the hydrogen runs at 380°C. In these runs 100 g. of carbide grains was used. The results are shown in Fig. 2,

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* At times the temperature at the reaction zone is nearly as much as 100°C higher than the average temperature (300°C) of the furnace.

(8) R. Negishi, a paper to be published in *Rev. Phys. Chem., Japan*, (1941). This precisely has been the case in the synthesis of iso-butyl alcohol in the presence of the carbide. By the continuous and rapid removal of the products of reaction, the equilibrium of the reaction is shifted sufficiently to counter-balance the effects of reduced pressure and temperature.

(9) According to K. Kawakita, *Rev. Phys. Chem., Japan*, **11** (1937), 75; *ibid.*, **12** (1938), 105; *ibid.*, **13** (1939), 87; ibid., *ibid.*, **14** (1940), 1, the reaction is, on a reduced iron catalyst,

1) $Fe+(CO_2)_{ads.} = Fe_xO_y+(CO)_{ads.}$

2) $2(CO)_{ads.} = C+(CO_2)_{ads.}$,

and these steps are repeated. This reaction can take place at a fairly low temperature range, 300 to 400°C.

(10) H. A. Taylor and A. van Hook, *J. Phys. Chem.*, **39** (1935), 811; J. B. Conn, G. B. Kistisakowsky, and E. A. Smith, *J. Am. Chem. Soc.*, **61** (1939), 1868; A. Farkas and L. Farkas, *ibid.*, **61** (1939), 3396. The latter authors have shown that acetylene is first hydrogenated nearly completely to ethylene, and the ethylene then is hydrogenated to ethane.

(11) G. Egloff and E. Wilson, *Ind. Eng. Chem.*, **27** (1935), 917. They claim that ethylene is the key molecule for the polymerization of organic products. including the unsaturated.

(12) Storch, *J. Am. Chem. Soc.*, **56** (1934), 374. He has explained the formation of olefins with odd carbon number from ethylene by assuming a disproportionation to give a higher and a lower olefin, for example,

$$C_2H_4 + C_4H_8 \begin{cases} \nearrow 2C_4H_6 \\ \searrow C_6H_{12} \end{cases}$$

which is self-evident and requires no further remarks, especially when in lack of more complete data on the subject.

Finally, a comment will be made on the size of carbide grains. In some of the runs with powdered carbide which are not mentioned in this paper, there has been some evidence that the reaction becomes too rapid due to local accumulation of the heat of reaction. The liquid yield, consequently, decreases markedly, and that of the decomposed carbon increases even more remarkably. If the size of the grains is too large, the surface available for reaction becomes less, and the concentration of the nascent acetylene molecules may become too small, and again the yield decreases. The same sort of concentration effect has been found when the saturation temperature is too low (about 65°C). On the other hand, when the temperature is above 85°C, and the concentration of the water molecules is large, the yield of liquid products has been reduced by the heat of reaction involving the water molecules and the carbide.

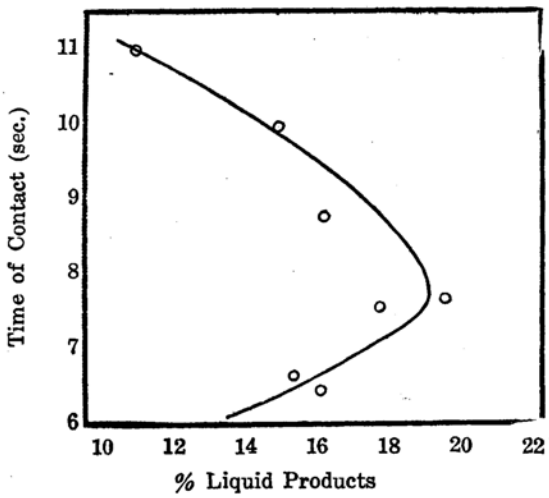

Fig. 2. Time of Contact and Yield.

With these informations on hand, studies on the synthesis of hydrocarbon liquids directly from the carbide have been continued, using such gases as CO_2, C_2H_2, water gas, and HCl, and their results will be given in the later papers which will appear also in this Bulletin.

Summary.

General experimental procedure, methods of analysis, and purification of materials have been given sufficiently in detail in order that the sources of difficulty and uncertainty in the results obtained not only in this paper but also in this series of investigations on the non-catalytic synthesis of hydrocarbon liquids directly from calcium carbide may be estimated.

Orientation and exploratory investigations have been made on hydrogen systems, and it has been found that a grain size of 1 to 2 mm, a saturation temperature of 80°C, and a reaction temperature of 340°C proved most suitable for the synthesis of liquid hydrocarbons under our experimental conditions.

The effects on the formations of the products of temperature have been discussed. These effects are intimately associated with the heat of reaction involving the carbide which is large.

The effects of the time of contact and of the grain size have been briefly mentioned in passing.

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