Hydrocarbons from Carbide (A) III.* Non-catalytic Polymerization under Ordinary Pressure. Carbon Dioxide-, Carbon Monoxide-, and Hydrogen Chloride-Calcium Carbide Systems.**

By Ryoji NEGISHI and Osamu KAMIIKE.

(Received January 12, 1942.)

In our first paper⁽¹⁾ of the present series, we have reported on the results of the orientation runs made with hydrogen and, with the informations gained therefrom, we have made a series of runs with carbon dioxide, water gas, and hydrogen chloride, singularly or with their mixtures, to increase further the yield of liquid products. Their results will be given in this paper. We shall reserve a fuller discussion on the results and on the mechanisms of the reaction in question for the third and final paper of this series of investigations on the non-catalytic polymerization under ordinary pressure.

I—Carbon Dioxide System.

We have chosen this system first, because we are reasonably certain that there will be no oil formation⁽²⁾ from the gas itself which probably

---

* This paper has been published by permission of Dr. M. Sato.

** The experimental details of these systems have been given in a series of papers published in Japanese in *J. Soc. Chem. Ind. Japan*, **44** (1941), 1028; ibid., **45** (1942), 133.

(1) R. Negishi and O. Kamiike, Paper (A) II, this Bulletin, **17** (1942), 118.

(2) F. Fischer, *Brennstoff-Chem.*, **10** (1929), 279. According to him, when acetylene is mixed with 10% CO_2, the yield of liquid products increases, but there is no reaction involving CO_2, except that only about 0.27% of it is transformed into CO and traces of water.

would not be the case with acetylene or with water gas, and we can ascribe the whole mechanism of the oil formation to nascent acetylene.

In this section of the paper, only those runs with carbon dioxide alone and its mixture with hydrogen will be dealt with, and the runs with hydrogen chloride will be given at the time the latter system is discussed.

Most of the runs were made at 340°C and some at higher temperatures only when the supplementary data were necessary. Experimental conditions are given in Table 3.* The apparatus, the procedure of run, and the materials used have already been given.⁽¹⁾ In this and the subsequent investigations of the series, however, "desorption," (so designated for want of a better term) has been effected as follows: after the reaction had been conducted for a given period of time, the reaction gas** was switched over from the saturator to the by-pass, and the dried gas was introduced into the reaction zone. The temperature of the furnace was then raised. When the temperature was raised above 400°C, the effect of desorption was evident, as shown by a large amount of condensation along the cooler parts of the reaction tube. When the amount of condensation became small, the temperature was lowered to the original point, and the gas was switched back to the saturator. This process was repeated as often as necessary, but usually two per run sufficed.

Table 1. Carbon Dioxide-Carbide System.

Exp. No.	$\mathrm{I_L}$37	$\mathrm{I_L}$40	$\mathrm{I_L}$41	$\mathrm{I_L}$57	$\mathrm{I_L}$59	$\mathrm{I_L}$60
React. Temp. (°C)	380–400	340–380	340–380	340	380	420
Gas	CO_2	CO_2+H_2	CO_2+H_2	CO_2	CO_2	CO_2
Saturation temp. °C . .	80	80	72	80.3	80.3	80.3
Ratio Gas to Water (partial Press.) . . .	1:0.85	$CO_2:H_2:H_2O$ 2:1:2.67	$CO_2:H_2:H_2O$ 1:1:1	1:0.86	1:0.87	1:0.87
Time of Contact (sec.) .	15.6	22.2	16.7	22.1	18.8	16.1
Liq. Prods. (g.)*** . . .	13.95	14.7	17.2	27.9	21.5	10.3
Water	10.9	13.0	3.8	9.0	29.4	18.8
Oil on Reacted (%) Carbide Acetylene . .	35.5	32.7	33.6	43.3	38.8	23.9
Oil on Reacted (%) Carbide Carbon . . .	31.20	29.6	31.1	41.0	35.7	22.21
Carbon Balance	96.6	98.5	95.6	99.6	97.7	—
Wt. Balance	98.1	98.3	99.7	99.3	100.2	95.0

200 g. of carbide was used in every run.

Results and Discussion. Out of a large number of runs, only those which are sufficiently accurate to give either the total weight balance or the carbon balance more than 95% are shown in Table 3. The results of the first three runs are less comparable, because they are more or less explorative in nature, and the reaction temperatures have been varied over a wide range. Those of the last three runs are, however, quite

---

* The numbering of the Tables and Figures are consecutive throughout the whole series of papers, from (A) II to the final one.

** When a different gas, for example, H_2 or CO_2, was used to effect desorption, the reaction gas was shut off, and the dry gas in question was introduced from the by-pass.

*** Hydrocarbons.

comparative, and some interesting and suggestive results are possible from them. As has been the case with our first report,⁽¹⁾ the maximum yield of liquid products is again at 340°C* and at higher temperatures it diminishes. The ratio of liquid products to water seems to decrease with an increase of temperature, even when the extent to which the carbide has reacted is taken into consideration.

The percentage of the liquid products have been calculated on two different bases, namely, one on the reacted carbide acetylene and the other on the reacted carbide carbon. This sort of calculation has been performed, because we are really interested in the total amount of the liquid products which can be obtained from the carbide, or acetylene, (it is what becomes of the acetylene that is pertinent). There is also another reason for making this calculation. If the products are hydrogenated, the percentage of the liquid products will increase in proportion to the degree of hydrogenation, since the total weight of the liquid products is considered on the acetylene basis, while on the carbon basis, it will remain the same. Therefore, by comparing the two sets of percentages, we can obtain some idea as to the extent to which the products are hydrogenated and some information with regard to the mechanism of the reaction. If the two sets of values are the same, it means that there is no hydrogenation, or that there is no product of which H/C ratio is greater than that of acetylene; in other words, the reaction is simply

$$nC_2H_2 = (C_2H_2)_n \; .$$

It is obvious from the results of Table 3 that the yield, calculated on acetylene, is always larger than that on the carbon. It may mean several things: either the whole products contain slightly more hydrogen than that in acetylene molecule or the majority of the products has about the same H/C ratio as that of acetylene, but there is present a small quantity of a substance with a very much higher H/C ratio. The data are not sufficiently accurate nor copious to decide which of the two is most probable, but the results of the elementary analysis in Table 4 are suggestive. It is rather surprising that the products contain so much oxygen. If it is assumed that most of it is due to methyl alcohol, which has been identified, we get some interesting results, as illustrated by I_L 57. Let us take the trap condensates of which elementary analysis gives the following results:

$$C = 74.98, \quad H = 9.37, \quad 0 = 15.65, \quad H/C = 0.1250.$$

Now, if we assume that all of this oxygen is due to methyl alcohol and make correction accordingly, the final H/C becomes 0.0853, while that of acetylene is 0.0833. The ratios of the percentages based on acetylene to those based on carbon are practically constant and greater than unity but slightly. From these facts we may assume reasonably that the majority of the products has a H/C ratio which is very nearly equal

---

* This seemed to be the case in the whole series of runs made under the ordinary pressure with the gases which are not themselves capable of polymerizing into liquid products. This point will become more clear when the results with other gases, especially acetylene, are reported later in this Bulletin.

to that of acetylene, but a small amount of substance with a higher ratio is also present. The main reaction of the nascent acetylene molecules, therefore, seems to be

$$nC_2H_2 = (C_2H_2)_n ,$$

whether H_2 (and CO_2) is present in the system or not.

Tabele 4. Gas Analysis (Carbon Dioxide-Carbide System).

Gas	I_L37 (%)	I_L40 (%)	I_L41 (%)	I_L57 (%)	I_L59 (%)	I_L60 (%)
CO_2	72.8	33.5	30.5	56.6	64.6	72.8
C_2H_2	10.5	17.4	8.4	18.8	22.2	12.1
C_2H_4	0.9	0.6	0.6	0.2	0.4	0.4
C_nH_{2n}	0.0	—	0.0	0.1	0.7	0.6
O_2	0.6	0.8	0.9	0.4	0.6	0.2
CO	0.6	0.6	0.6	0.3	0.8	0.4
H_2	7.4	41.2	50.4	18.3	5.8	8.3
CH_4	3.5	2.2	1.9	2.2	2.4	3.3
N_2	4.0	3.5	3.9	4.0	2.8	2.4

The first striking thing about the results of elementary analysis in Table 4 is, as has been mentioned above, the high content of oxygen in the products, especially in the trap. Just what sort of oxygen we have here is at present difficult to say, but some evidence indicates that it is predominantly alcoholic. When the last three results in Table 4 are compared, it is interesting and may be of significance, that, both in the trap and condenser, the carbon content increases, while H/C ratio and the oxygen content decrease, respectively, with increasing temperature. When the analysis of the liquid products becomes more complete, we may be able to give a proper interpretation of the results.

In Table 5 the results of gas analysis are given. They should be considered qualitatively rather than quantitatively, since they do not represent the real compositions of the effluent reaction gas, owing to the fact that part of the effluent gas during desorption is invariably mixed with the effluent reaction gas. As for example, a high content of hyrogen in I_L 57 is due, undoubtedly, to the circumstance that desorption has been effected with hydrogen. Even with this limitation, a general trend in the change of the composition with temperature is as has been found in Paper (A) II⁽¹⁾ when the last three runs are compared.

There may remain some doubt as to the real significance of desorption, as defined in this paper, and in order to remove it I_L60 has been made. It became clearer from the results of this paper and those of a number of unpublished data that most of the liquid products were desorbed at near 420°C. If the apparent increase in the yield at the time of desorption is due rather to the increase in the oil formation at higher temperatures, the total yield should be higher for the reaction made at about 420°C than at lower temperatures. The data in Table 3 clearly indicate that the increase in the yield is due to a more efficient liquid formation at lower temperatures plus the effect of desorption, and not due to that of higher reaction temperature.

Table 5. Elementary Analysis (Carbon Dioxide System).

Element		I_L37 Combined	I_L40		I_L41		I_L57		I_L59		I_L60	
			Trap	Cond.	Trap	Cond.	Trap	Cond.	Trap	Cond.	Trap	Cond.
C(%)	..	81.23	78.66	84.92	83.02	84.02	74.62	83.19	77.43	85.75	80.56	86.59
H ”	..	8.62	9.93	8.53	10.10	8.46	9.96	8.76	10.24	8.60	9.76	8.49
C ”	..	10.15	11.41	6.35	6.88	7.52	15.42	8.05	12.32	5.65	9.68	4.92

Finally, the results of the present work indicate that the only reaction in which carbon dioxide is involved is that of the formation of carbonate, in agreement with the observations of Fischer⁽²⁾. Run I_L40 illustrates this point effectively. In this calculation the following have been assumed: (a) only acetylene forms the liquid, higher polymers, other gases (olefines and saturated), and free carbon; (b) the originally contained carbonate does not take part in any reaction. The results of calculation are gratifying.

Source of Carbon	Introduced (g.)	Found							Balance
		Free Gas (g.)	Decomp. +High Polym. (g.)	Carbonate (g.)	Liquid (g.)	Other Gases (g.)	Unreacted (g.)	Sum (g.)	
C_2H_2	62.92	13.84	12.64	——	12.36	1.49	21.28	61.61	1.31
CO_2	30.10	13.30	——	16.76	——	——	——	30.06	0.04
Carbonate ..	1.17	——	——	1.17	——	——	——	1.17	(0.0)

II—Carbon Monoxide System.

In this system we have investigated the effect of a carrier gas which is itself capable of forming liquid products. From the studies of the hydrogen and of the carbon dioxide systems, we have obtained some indications that the main reaction of nascent acetylene is not influenced by carrier gases. It has been hoped, therefore, that it may be possible to effect a typical Fischer-Tropsch reaction (in the absence of a catalyst for the reaction) in parallel with the main reaction of the carbide.

The experimental results are given in Table 6 in which I_L62, of which weight balance deviates by more than the usual limit, ±5%, has been included for the sake of comparison. It must be added here that we have had a great deal of experimental difficulty with this system. Quite frequently the reaction tube cracked without any warning, and although we had made quite a number of runs with CO alone and with its mixtures, only the two, given in the Table, appeared sufficiently quantitative. It may also be mentioned that for every run that appears in the Table, at least five runs have been made that are not sufficiently quantitative and are, therefore, not shown in the Table. Recourse to them, however, will be freely made in our discussion.

Table 6. Carbon Monoxide-Carbide System. Hydrogen Chloride-Carbide System.

Exp. No.	I_L44	I_L50	I_L64	I_L65	I_L62
Reaction Temp.(°C) .	340	340	340	340	380
Gas	CO	$CO+H_2$	CO_2+HCl	CO_2+HCl	H_2+HCl
Saturation Temp.(°C)	80.1	72.5	79.3	80	90.5
Ratio Gas to Water (Partial Press.) . .	$CO:H_2O$ 1:0.85	$CO:H_2:H_2O$ 2:4:3	$HCl:CO_2:H_2O$ 0.1:409:347	$CO_2:H_2O$* 1:0.86	$HCl:H_2:H_2O$ 174:311:275
Time of Contact (sec.)	19.0	29.3	21.4	26.7	23.9
Liq. Prods. (g.) . . .	6.4	5.2	23.7	19.2	7.7
Water (g.)	3.0	0.4	17.2	13.6	27.15**
Oil on Reacted (%) Carbide Acetylene.	10.3	22.0	39.9	38.9	31.6
Oil on Reacted (%) Carbon (Carbide) .	10.2	20.3	33.2	35.1	27.6
Carbon Balance . . .	102.0	98.3	97.4	96.5	–
Weight Balance . . .	100.6	100.5	98.3	96.1	81

200 g. of calcium carbide grains was used in every run.
* Traces of HCl.
** $H_2O+23.9\%$ HCl.

Before we made the experiments, we had hoped, according to our thermodynamic calculations(3), that we might obtain a larger total yield of liquid products by using water gas as a carrier gas, but our experimental results seemed to point otherwise. In fact, they indicated that the gas not only failed to form any liquid,* but had actually decreased** the yield, as shown in Table 6. The small yield might have been due to the fact that in these runs no desorption has been effected, but this can account only for a small part, since it is shown that the effect is appreciable only when CO_2 is involved as in I_L64. We are at present unable to offer a comforting explanation for the harmful effect of carbon monoxide or water gas on the direct synthesis of hydrocarbon liquids from the carbide.

The results of gas analysis in Table 7 should be considered rather qualitatively than quantitatively for the same reasons given in connection with CO_2 system. The results of semi-quantitative calculation, based on the gas analyses of I_L44 and I_L50, showed that part of the original CO had reacted to form CO_2 (eventually it produced calcium carbonate) and methane, but no liquid products.

---

(3) R. Negishi, O. Kimura, and O. Kamiike, *Rev. Phys. Chem., Japan*, **15** (1941), 31, Paper (A) I.

* I_L47 was made to see whether the carbide had any effect on a dry $CO+H_2$ mixture of 1:2 proportion or not. The temperature was varied from 150°C to 450°C, but there was no liquid formation; moreover, there was but slight reaction of any sort, as indicated by the negligible change in the weight of the carbide before and after the reaction (from 200 to 200.5 g.) and by the results of gas analysis (gas at 300°C) shown in Table 7. The original composition was about the same as that of I_L50.

** For I_L52, made under the same conditions as those of I_L50, the yield of liquid was 20.0%.

Table 7. Gas Analysis.

Gas	I_L44 Reacted (%)	I_L44 Introd. (%)	I_L50 Reacted (%)	I_L50 Introd. (%)	I_L64 (%)	I_L65 (%)	I_L62 (%)	I_L47 (%)
CO_2	0.67	0.9	0.47	—	71.26	76.7	2.48	1.8
C_2H_2	8.75	—	6.20	—	15.68	16.9	6.77	1.0
C_2H_4	0.37	—	0.43	—	0.58	0.4	0.64	0.4
C_nH_{2n}	0.30	—	0.37	—	0.37	0.2	0.50	0.0
O_2	0.51	—	0.80	—	0.32	0.4	0.94	1.4
CO	71.34	99.2	23.88	31.6	0.48	0.2	0.54	28.2
H_2	9.28	—	60.54	61.9	6.90	2.3	80.89	58.8
CH_4	3.75	—	1.70	—	2.33	1.2	4.74	2.0
N_2	5.15	—	6.00	6.3	2.58	2.4	2.34	6.4

III—Hydrogen Chloride System.

Hydrogen chloride has been used to investigate the effect on the yield of the destruction of the basic substances produced in the reaction and the catalytic effect—if any—of the acid.

The effect of hydrogen chloride vapors seemed but slight. Although there was some difference in the physical appearance of the liquid products in runs I_L62 and I_L64, it might very well be accounted for by other effect than that of the acid concentration.* We hesitate to make a definite conclusion as to the effect on the yield of liquid products of the acid and also of the carbonate, but the results of Tables 8 and 9 are suggestive.

Table 8. Carbonate Carbon in Residue.

Exp. No.	Wt of Residue (g.)	CO_3 Carbon in Residue (g.)	CO_3 Carbon on React. CaC_2 Carbon (%)
I_L64	288.1	27.46	47.5
I_L62	277.4	2.67	10.4
I_L65	283.3	23.43	47.5
I_L57	389.9	25.91	46.3

Table 9. Effect of Acid on Liquid Yield (at 340°C).

Exp. No.	HCl Conc. Wt. (%) Average	Vap. Press. mm Hg HCl	 H_2O	 CO_2	Liquid Carbon on React. Carbide Carbon (%)
I_L62*	26	174	267	324*	28
I_L64	3.5	0.1	347	409	33.2
I_L65	0.58	Trace	350	410	35.1
I_L57	0.0	0.0	350	410	41.0

* At 380°C; instead of CO_2, H_2 was used.

---

* The concentration of HCl in the saturated vapor was computed from the partial vapor values given in Int. Crit. Tables, Vol. III (1928), 301. Its concentration in the vapor phase was expressed in mm Hg and that in the liquid by weight percent, determined by titration with Na_2CO_3.

In Table 10 the results of elementary analysis of the liquid products are given. It seems that the products formed in the presence of CO contain less oxygen while those formed in the presence of the acid contain larger amounts than those with carbon dioxide. A proper explanation also awaits for this peculiar effect, if real.

Table 10. Elementary Analysis.

Element	I_L44		I_L50	I_L64		I_L65		I_L62	
	Trap	Cond.	Combined	Trap	Cond.	Trap	Cond.	Trap	Cond.
C(%)	82.02	84.60	85.20	74.29	79.79	67.70	84.96	——	81.63
H "	9.71	8.69	8.76	10.10	8.78	10.48	8.85	——	8.20
O "	8.27	6.71	6.04	15.61	11.43	21.82	6.19	——	10.17

Summary.

The effects on the synthesis of hydrocarbon liquids directly from calcium carbide, in the temperature range of 340 to 420°C, of carbon dioxide, carbon monoxide, hydrogen choride, and their mixtures have been studied. The present results are in general agreement with those of the hydrogen system, and it has been found that the main reaction of the nascent acetylene molecules is but slightly affected by the carrier gases.

In the carbon dioxide system the yield of liquid products has been found as high as 43% of the total reacted acetylene. The only reaction in which carbon dioxide takes part is the formation of calcium carbonate. The presence of hydrogen seems to have no effect on the character of the liquid products.

It has been shown that while carbon dioxide has favourable, carbon monoxide has unfavourable effects, and hydrogen chloride has none at all, or but slight, on the liquid yield.

In the presence of the carbide and its reaction products, carbon monoxide with hydrogen does not effect a Fischer-Tropsch synthesis; however, it reacts to produce some carbon dioxide and methane.

The Central Laboratory,
South Manchuria Railway Company, Dairen.