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Hydrogenation and Polymerisation Reactions of Acetylene. I. The Reaction in Liquid Phase and the Effect of High Tension Discharge.

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Many experiments have been carried out on the hydrogenation and polymerisation of acetylene to obtain gaseous and liquid hydrocarbons. The hydrogenation reaction to obtain ethylene has been studied by Paal and Hoheneggen(1), Ross and his collaborators(2), and K. Yoshikawa(3), while the polymerisation reaction in the presence of hydrogen to obtain liquid hydrocarbons has been studied by Fischer and Peters(4), Petrov and Antzus(5), Ackerman(6), K. Shiomi(7), and Amemiya(8). The results of these investigations suggest us that the above reactions can hardly be separated and the one reaction is always accompanied by the other. This tendency is not desirable from the industrial standpoint, and consequently many devices, such as the dilution of the catalyst with the carrier or the performance of the reaction in liquid phase, have been tried to separate the reactions, but the problem is not yet solved.

Now let us consider why these two reactions cannot be separated. The reactions of acetylene in the presence of hydrogen can be classified in three types. The first is the hydrogenation of acetylene, and there exist two reactions:

$$C_2H_2 + H_2 \rightarrow C_2H_4$$

$$C_2H_2 + 2\,H_2 \rightarrow C_2H_6\,.$$

The second is the polymerisation reaction and this reaction includes many types, among them the typical one is

$$3\,C_2H_2 \rightarrow C_6H_6\,.$$

The third is the decomposition reaction of acetylene:

$$C_2H_2 \rightarrow 2\,C + H_2\,.$$

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(1) *Ber.*, **48** (1915), 275.
(2) *J. Ind. Eng. Chem.*, **13** (1921), 775.
(3) *Bull. Chem. Soc. Japan*, **6** (1932), 201.
(4) *Brenn-Chem.*, **12** (1931), 286.
(5) *J. App. Chem.*, **12** (1937), 357.
(6) *Brenn-Chem.*, **18** (1937), 357.
(7) *J. Soc. Chem. Ind. Japan*, **41** (1938), 831.
(8) *Ibid.*, **42** (1939), 692.

Besides these reactions, there also exist secondary ones, e.g., the polymerisation of ethylene to give olefins and the formation of methane by the combination of decomposed free carbon and hydrogen. Now, to know the energetic relation of these reactions, the free energies of formation are shown in Fig. 1. As seen in Fig. 1, these reactions are always accompanied by remarkable diminution of free energy between 0°C and 500°C.

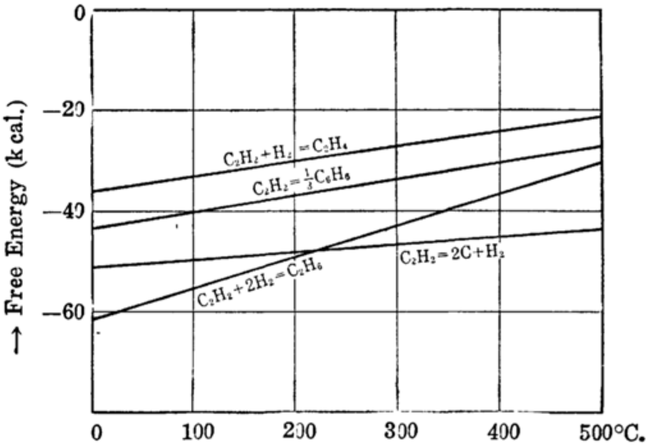

Fig. 1. Free Energies of Formation.

Next, let us consider these reactions from the standpoint of chemical kinetics. According to Pease⁽⁹⁾, the polymerisation of acetylene is a second order homogeneous reaction, and the first step of the reaction is proposed by Zelinski⁽¹⁰⁾ to be

$$2\,C_2H_2 \rightarrow (C_2H_2)_2\,.$$

Taylor and van Hook⁽¹¹⁾ confirmed that the reaction is of second order, and obtained the activation energy of 40,000 cal. The hydrogenation reaction of acetylene was also studied by Taylor and van Hook⁽¹¹⁾, and they found that activation energy of this reaction was 42,000 cal. These results show us that the activation energies of these two reactions are very near, if not equal. As to the decomposition reaction to form free carbon and hydrogen, precise investigation is not yet reported. The fact that the activation energies of polymerisation and hydrogenation are nearly equal conforms with the experimental result that these two reactions can hardly be separated. Circumstances may become somewhat different when a catalyst exists. From many experiments it is believed that acetylene is more easily and firmly adsorbed on metallic surface than hydrogen. Farkas and Farkas⁽¹²⁾ confirmed it on platinum surface by measuring the ortho- para conversion of hydrogen. Owing to this, it is not difficult to suppose that polymerisation reaction predominates, provided that the hydrogen concentration is not too high. The above supposition is confirmed by experiments with some exceptions⁽³⁾. The present author formerly tried to obtain liquid hydrocarbons by the direct reaction of water vapour and hydrogen on calcium carbide, and tried the thermo-

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(9) *J. Amer. Chem. Soc.*, **51** (1929), 3470.
(10) *Ber.*, **57** (1924), 264.
(11) *J. Phys. Chem.*, **39** (1935), 811.
(12) *J. Am. Chem. Soc.* **61** (1939), 3396.

dynamical calculations(13). A special feature of this trial consists in untilizing the enormous reaction heat of water vapour and calcium carbide and facilitating the hydrogenation and polymerization reactions. The results showed us, however, that the polymerisation reaction was accerelated too much owing to the high activity of acetylene, and the reaction product was high polymer such as tarry substances or cuprene.

Generally, in a reaction which is accompanied by enormous evolution of heat such as in our case, local over-heating at the reaction zone is inevitable. It is not difficult to suppose that an unstable substance such as acetylene is very sensitive to temperature; therefore, if we want to control such reactions, strict homogenuity of temperature must be fulfilled. A method to satisfy this condition is to carry out the reaction in liquid phase. For this reason the polymerisation and hydrogenation reactions of acetylene were studied in liquid paraffin in the presence of catalyst and it is described in the first half of this paper. Similar investigation was carried out by Fischer and Peter(4), using nickel and copper as catalyst, in which only gas contractions are recorded but little remarks on the nature of the reaction are made. In this paper, the results of the reaction in the presense of such catalysts as nickel, cobalt, palladium, and copper are described with some considerations concerning the nature of the reaction.

To obtain liquid fuel from acetylene, it is desirable that appropriate hydrogenation and polymerisation reactions occur at the same time, but, as was stated above, polymerisation reaction occurs more easily than hydrogenation reaction when a catalyst such as nickel is present. To avoid this defect, the activation of hydrogen is desirable. Under these considerations, the present author tried the hydrogenation and polymerisation reaction in liquid phase under the influence of high tension electric discharge. The effect of high tension discharge on the hydrogenation reaction of several organic substances was studied by I. Seto(14), and a considerable acceleration of hydrogenation was found. This effect was attributed to the activation of hydrogen. Under these conditions, it is supposed that the hydrogenation may be accelerated to some extent, local heating being avoided owing to the surrounding liquid medium. The results are described in the latter half of this paper.

Part I. Reaction in Liquid Phase.

Apparatus and Experimental Procedures. The apparatus is shown in Fig. 2. A mixture of acetylene and hydrogen was reserved in a 20 litre glass bottle and flowed into a reaction vessel at a constant speed, passing through a flowmeter and a calcium chloride tube. The reaction vessel was made of Pyrex glass, 3.5 cm. in diameter and 25 cm. in height. At its bottom there was a glass filter through which the gas mixture bubbled up. The resulting gas was first freed from light oil in a trap and then led into a gas-meter. The reaction vessel was kept at a constant

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(13) Negishi, Kimura, and Kamiike, *Rev. Phys. Chem. Japan*, **15**(1941), 31.

(14) *J. Soc. Chem. Ind. Japan*, **40**(1937), 388; **42**(1930), 555.

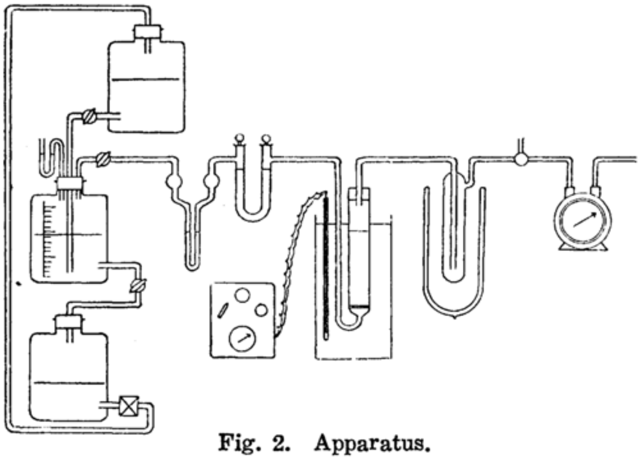

Fig. 2. Apparatus.

temperature by means of a temperature regulator; the temperature fluctuation of which was less than ±5°C. The analysis of gaseous product was carried out according to the method of Schuftan(15).

Acetylene is prepared from calcium carbide and water, and then washed with potassium chromate solution, acidic copper sulphate solution, and then with alkaline pyrogallol solution. The hydrogen used is commercial electrolytic hydrogen in a bomb, and it is washed with a pyrogallol-potassium hydroxide solution to remove oxygen. The proportion of acetylene and hydrogen is 1:1 throughout these experiments. The catalysts used are nickel, cobalt, palladium, and copper. The method of preparation of nickel catalyst is as follows: From nickel nitrate solution and sodium carbonate solution, nickel carbonate is precipitated. It is thoroughly washed and dried. Fomic acid is added to it, and then dried at 100°C in an air-bath. The product is nickel formate. Five grams of nickel formate is mixed with 100 c.c. of liquid paraffin and is reduced with hydrogen at 250°C., in the reaction vessel. In two hours the reduction is complete, according to the following equation:

$$\mathrm{Ni(HCOO)_2} \rightarrow \mathrm{Ni} + \mathrm{H_2} + 2\mathrm{CO_2}.$$

The superior activity of the catalyst thus prepared was studied and stressed by Eger and others(16). The method of preparation of cobalt catalyst is as usual. Cobalt carbonate is deposited on kieselguhr by adding sodium carbonate solution on cobalt nitrate solution, and then the precipitate is thoroughly washed and dried. Six grams of it, containing 3 g. of cobalt, is reduced at 350°C. with hydrogen during three hours, and then 100 c.c. of liquid paraffin is poured on it in the atmosphere of hydrogen. Palladium catalyst is prepared from palladium chloride solution, into which kieselguhr is added, by reducing with a formaldehyde solution. Four grams of it, containing 1 g. of palladium, is mixed with 100 c.c. of liquid paraffin. Copper catalyst is prepared by reducing copper oxide, which is deposited on kieselguhr as copper hydroxide, with hydrogen three hours at 250°C. Six grams of it, which contains 3 g. of copper, is mixed with 100 c.c. of liquid paraffin in the atmosphere of hydrogen.

Results of Experiment. The results of the experiments are tabulated in Tables 1–4, and the contraction ratios of gases are graphically shown in Fig. 3.

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(15) "Gasanalyse in der Technik," Leipzig (1931). O. Kamiike, *et al.*, *J. Soc. Chem. Ind. Japan*, **44** (1941), 1030.

(16) "Die Hydrierung mit Nickelformiate als Katalysator," (1931).

Table 1. Experimental Results with Nickel Catalyst.

Temp. (°C.)	75	100	125	150	175	200
Acetylene:hydrogen	1:1	”	”	”	”	”
Flow velocity (l./h.)	3.5	4.0	4.0	4.0	4.0	4.0
Gas flowed in (l.)	2.5	2.0	2.5	2.0	2.0	2.0
Gas flowed out (l.)	2.45	1.90	2.15	1.44	1.27	1.12
Contraction ratio (%)	2	5	14	27	37	44
Gas Analysis (%):						
CO_2	0.6	1.1	1.1	0.8	1.0	0.9
C_2H_2	47.6	44.5	39.0	30.9	28.1	23.0
C_2H_4	0.4	0.2	1.5	2.9	3.0	4.6
C_nH_m	0.1	0.5	2.0	4.0	7.1	9.1
O_2	0.3	0.0	0.0	0.0	0.0	0.0
CO	0.5	0.0	1.1	0.8	1.2	0.7
H_2	48.1	49.3	50.7	53.7	52.0	54.2
CH_4	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0
N_2	3.4	7.3	5.6	6.9	7.6	7.5
Value of M (%)	64	78	67	72	77	72

Table 2. Experimental Results with Cobalt Catalyst.

Temp. (°C.)	100	150	200	250
Acetylene:hydrogen	1:1	”	”	”
Flow velocity (l./h.)	2.0	2.5	2.5	2.0
Gas flowed in (l.)	3.0	3.0	3.0	3.0
Gas flowed out (l.)	2.85	2.55	2.1	1.89
Contraction ratio (%)	5	15	30	37
Gas Analysis (%):				
CO_2	1.9	1.4	1.4	1.1
C_2H_2	44.4	44.7	39.9	35.5
C_2H_4	0.0	0.1	0.7	1.7
C_nH_m	0.0	0.7	2.5	5.2
O_2	1.0	0.6	0.7	0.0
CO	1.2	0.5	0.8	0.0
H_2	46.1	47.6	47.8	50.3
CH_4	0.0	0.0	0.0	0.0
C_2H_6	0.0	0.0	0.0	0.0
N_2	5.4	4.4	6.2	6.2
Value of M (%)	80	84	78	72

Table 3. Experimental Results with Palladium Catalyst.

Temp. (°C.)	50	100	125	150	175	200	225
Acetylene:hydrogen	1:1	”	”	”	”	”	”
Flow velocity (l./h.)	3.5	3.5	3.5	3.5	3.7	4.0	4.0
Gas flowed in (l.)	3.0	3.0	3.0	3.0	3.0	3.0	2.0
Gas flowed out (l.)	2.7	2.02	1.47	1.44	1.34	1.36	1.02
Contraction ratio (%)	10	33	51	52	55	55	50
Gas Analysis (%):							
CO_2	1.0	0.0	0.0	0.2	0.0	0.0	0.0
C_2H_2	44.1	22.8	12.1	2.1	2.0	2.4	2.3
C_2H_4	1.9	6.9	12.1	13.2	9.3	12.3	9.7
C_nH_m	2.0	19.7	30.7	25.9	28.6	34.6	25.4
O_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO	0.6	2.0	4.2	6.3	4.5	7.3	7.5
H_2	47.2	38.8	28.7	15.9	14.2	14.3	11.1
CH_4	0.0	2.2	0.1	23.2	25.5	26.0	28.5
C_2H_6	0.0	0.0	10.0	4.0	4.6	0.7	7.5
N_2	3.2	7.6	7.8	9.3	2.2	3.2	8.0
Value of M (%)	12	5	10	10	20	18	10

Table 4. Experimental Results with Copper Catalyst.

Temp. (°C.)	100	150	200
Acetylene:hydrogen	1:1	”	”
Flow velocity (l./h.)	3.0	3.5	3.5
Gas flowed in (l.)	2.5	2.0	2.0
Gas flowed out (l.)	2.3	1.75	1.56
Contraction ratio (%)	8	13	22
Gas Analysis (%):			
CO_2	1.0	0.7	0.8
C_2H_2	39.0	33.0	24.8
C_2H_4	0.0	0.2	1.0
C_nH_m	0.4	0.4	1.1
O_2	0.6	1.0	0.0
CO	0.1	0.0	1.3
H_2	50.4	56.3	64.5
CH_4	0.0	0.0	0.0
C_2H_6	0.0	0.0	0.0
N_2	9.5	8.4	6.5
Value of M (%)	92	98	90

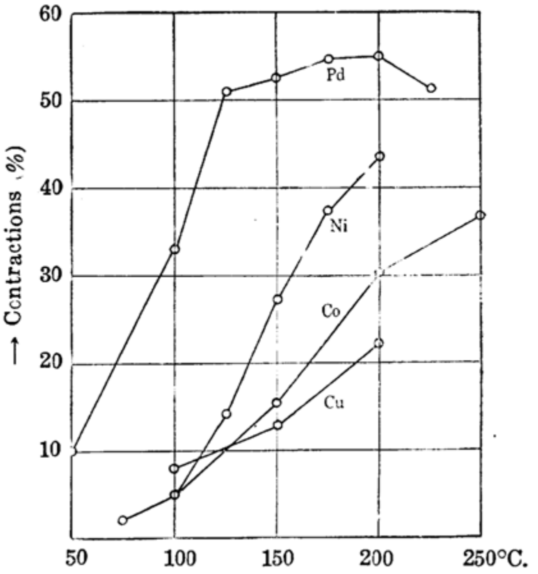

Fig. 3. Gas Contractions.

From Tables 1 to 4, it is seen that palladium catalyst is most active and the reaction takes place at the temperature as low as 50°C, while in the case of other catalysts, it is necessary to elevate the temperature at least up to 100°C. The nature of the reaction is also characteristic in each case, which can be seen from the data of gas analysis. In the case of palladium catalyst, the gaseous hydrocarbons other than acetylene, especially in ethylene and higher olefins. With the other catalysts, however, the gaseous hydrocarbons other than acetylene are very poor, especially in copper catalyst. In the case of copper catalyst, solid matter was found in the reaction vessel, which may presumably be cuprene. In each case the deposition of free carbon was scarcely found in the range of temperature of this experiment. From gas contraction curve, it is seen that in palladium catalyst, there exists a maximum contraction at about 180°C, while in other catalysts, such a tendency is not seen so far as is studied in our experiments. As is stated above, in palladium catalyst, the reaction product is rich in gaseous hydrocarbons, while in the other catalysts, it is poor in them; that is to say, the reaction product is rich in liquid hydrocarbons. To see this difference more quantitatively, the oilification ratio (M), that is to say, the ratio of liquid product to the total reaction product (gaseous and liquid), was calculated and shown in the last columns of Tables 1–4. In the calculation, it was assumed that C_nH_m contains four carbons on the average, which may not be so different from the case. In the case of copper catalyst, solid product was calculated as a liquid. As seen in Tables 1–4, in palladium catalyst, the M value is 5–20%; that is to say, 5–20% of the reacted acetylene is converted into liquid hydrocarbons, and 80–95% to gaseous hydrocarbons. Similarly, this value is 64–77% for nickel catalyst, 72–84% for cobalt catalyst, and 90–98% for copper catalyst. These figures show that in palladium catalyst, gaseous products are mainly obtained, while in nickel and cobalt catalysts, the product is mainly liquid, and in copper catalyst, liquid or solid. In general, M value does not depend on temperature so much.

Part II. Reaction under the Influence of High Tension Discharge.

The experimental results of part I show that hydrogen content in the reacted gases is generally much greater than acetylene, which means that the hypdrogenation reaction is slower than the polymerisation reaction of acetylene. This fact conforms with what is stated in the theoretical considerations. In order to obtain liquid fuel from acetylene and hydrogen, it is desirable that hydrogenation takes place in parallel with polymerisation. To fulfil this condition, the activation of hydrogen is necessary. The reaction was, therefore, carried out under the influence of high tension electric discharge, the significance of which was shortly stated in the introduction.

Apparatus and Experimental Procedures. The apparatus used is quite the same as shown in Fig. 2, except the reaction vessel, which is shown in Fig. 4. It is made of Pyrex glass, the height and the diameter being 23 cm. and 2.5 cm., respectively. At the center is provided an electrode, which serves as the inlet of reacting gas at the same time. Another electrode is a copper plate surrounding the reaction vessel. The diameter of inner electrode is 1.4 cm. and the distance between inner and outer electrodes is 0.5 cm. The reaction vessel is dipped in an oil-bath, the temperature of which is controlled by an automatic temperature regulator. As the high tension source an alternative current was used, which was obtained by a step-up transformer. The voltage was 25 kilovolts throughout the experiment and the current was less than 1 ma. As liquid medium liquid paraffin of high boiling point was used. The experiment was carried out with and without catalyst. Reduced nickel was used as catalyst. The method of preparation is as follows: Nickel carbonate is deposited on kielseguhr by addition of solium carbonate solution on nickel nitrate solution. The precipitate is thoroughly washed and dried, and then reduced with hydrogen during 2 hours at 300°C in the reaction vessel. The reduced nickel-kieselguhr catalyst is then suspended

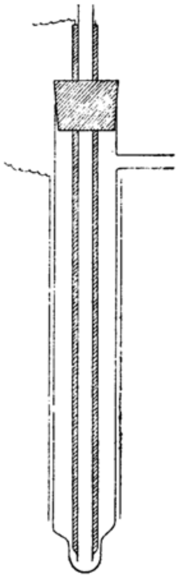

Fig. 4.

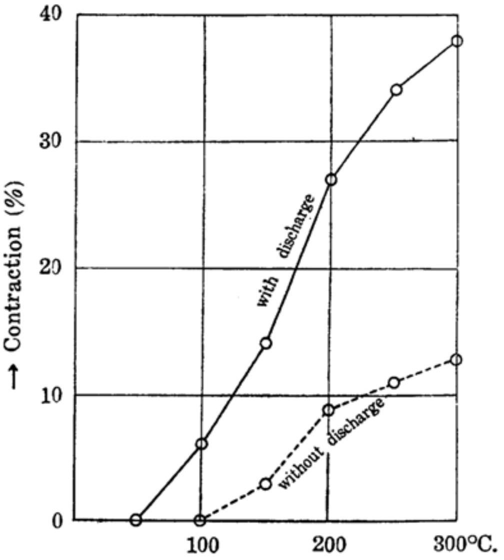

Fig. 5. Gas Contractions without Catalyst.

in 40 c.c. of liquid paraffin in the atmosphere of hydrogen. The catalyst used was 2 g. which contained 1 g. of nickel.

Results of Experiment. Experiment was first carried out without catalyst. In the reaction vessel only liquid paraffin was contained and the reacting gas was passed through it. The gas contractions and the analysis of resulting gases with and without high tension discharge are shown graphically in Fig. 5 and tabulated in Table 5, respectively.

Table 5. Experimental Results under the Influence of High Tension Discharge without Catalyst.

(Without High Tension Discharge)

Temp. (°C.)	50	100	150	200	250	300
Acetylene:hydrogen	1:1	”	”	”	”	”
Flow velocity (l./h.)	2	”	”	”	”	”
Gas flowed in (l.)	3.0	2.5	3.5	2.8	4.6	3.5
Gas flowed out (l.)	3.0	2.45	3.4	2.35	4.1	3.04
Contraction ratio (%)	0	2	3	9	11	13
Gas Analysis (%):						
CO_2	0.6	0.5	0.3	0.8	0.7	0.9
C_2H_2	45.4	45.6	43.2	38.4	40.1	35.3
C_2H_4	0.0	0.0	0.9	1.2	3.1	3.7
C_nH_m	0.0	0.0	1.1	1.6	0.4	1.2
O_2	0.6	0.6	0.0	0.0	0.0	0.0
CO	0.4	0.4	0.8	0.9	0.4	0.2
H_2	48.1	49.2	47.5	50.2	47.3	54.2
CH_4	0.0	0.0	0.0	0.0	0.0	0.8
C_2H_6	0.0	0.0	0.0	0.0	0.0	1.3
N_2	4.8	3.5	6.2	6.9	8.0	2.1

(With High Tension Discharge)

Temp. (°C.)	50	100	150	200	250	300
Acetylene:hydrogen	1:1	”	”	”	”	”
Flow velocity (l./h.)	2	”	”	”	”	”
Gas flowed in (l.)	2.7	2.8	3.5	2.35	2.25	2.6
Gas flowed out (l.)	2.7	2.65	3.0	1.72	1.48	1.62
Contraction ratio (%)	0	6	14	27	34	38
Gas Analysis (%):						
CO_2	0.2	0.4	0.1	0.5	0.5	0.8
C_2H_2	45.2	42.1	42.3	34.0	31.2	25.6
C_2H_4	0.2	0.2	1.2	1.8	3.8	6.3
C_nH_m	0.0	0.1	1.2	1.8	3.1	4.0
O_2	0.0	0.0	0.0	0.0	0.0	0.0
CO	1.4	0.7	0.9	2.5	1.4	0.5
H_2	47.7	45.4	48.2	50.3	52.6	52.9
CH_4	0.0	0.0	0.0	0.0	0.0	3.1
C_2H_6	0.0	0.0	0.0	0.0	0.0	2.8
N_2	2.9	6.7	7.1	9.1	7.4	4.0

In this experiment, only the reaction temperature was changed and other factors were maintained constant, viz., the ratio of hydrogen and acetylene was 1:1, the flow velocity of gas 2 l/hr., and the voltage of discharge 25 kilovolts. As seen in Fig. 6, the difference between the contraction ratios with and without high tension discharge is very remarkable, viz., about three times larger when discharge is present. The result of gas analysis shows that the amount of hydrogenated products (C_2H_4 and C_nH_m) are larger when discharge is present, especially at high temperatures. These facts show that the high tension discharge accelerate the hydrogenation as well as polymerisation reaction.

Next, the experiment was carried out when nickel-kieselguhr catalyst was present. The results of gas analysis are shown in Table 6, and the gas contractions in Fig. 6, graphically. In Fig. 6, we see that the gas

Table 6. Experimental Results under the Influence of High Tension Discharge with Nickel Catalyst.

(Without High Tension Discharge)

Temp. (°C.)	20	50	100	150	200	250	300	350
Acetylene:hydrogen	1:1	”	”	”	”	”	”	”
Flow velocity (l./h.)	2	”	”	”	”	”	”	”
Contraction ratio (%)	3	5	10	20	32	44	51	53
Gas Analysis (%):								
CO_2	0.2	0.4	0.6	0.8	0.5	0.0	0.8	0.3
C_2H_2	37.5	38.2	42.9	43.1	39.5	18.9	16.1	2.5
C_2H_4	0.8	0.7	0.5	0.5	0.9	4.3	5.8	7.3
C_nH_m	0.2	0.4	0.3	0.6	1.1	5.3	4.1	9.5
O_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO	0.7	0.9	0.6	1.4	0.3	0.5	0.8	0.4
H_2	52.8	50.9	47.3	47.3	51.4	68.1	68.9	62.8
CH_4	0.0	0.0	0.0	0.0	1.3	6.7	5.5	8.8
C_2H_6	0.0	0.0	0.0	0.0	1.8	3.8	5.9	4.3
N_2	7.8	8.5	7.2	6.3	3.2	2.4	2.1	3.1

(With High Tension Discharge)

Temp. (°C.)	20	50	100	150	200	250	300	350
Acetylene:hydrogen	1:1	”	”	”	”	”	”	”
Flow velocity (l./h.)	2	”	”	”	”	”	”	”
Contraction ratio (%)	5	5	12	26	41	50	55	57
Gas Analysis (%):								
CO_2	0.1	0.4	0.9	0.5	0.6	0.8	0.6	0.5
C_2H_2	36.0	36.6	39.4	35.7	47.3	35.5	34.0	25.3
C_2H_4	0.3	0.5	1.3	1.1	2.1	2.5	2.0	7.0
C_nH_m	0.5	1.1	0.4	0.9	1.5	1.4	4.4	2.3
O_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO	3.8	5.3	1.1	0.8	0.9	0.8	1.5	1.2
H_2	48.4	45.3	51.7	52.8	49.5	51.2	50.5	51.3
CH_4	0.0	0.0	0.0	0.0	0.0	4.3	2.6	1.9
C_2H_6	0.0	0.0	0.0	0.0	0.0	1.5	1.3	6.8
N_2	10.9	10.8	5.2	9.2	8.1	2.0	3.1	3.3

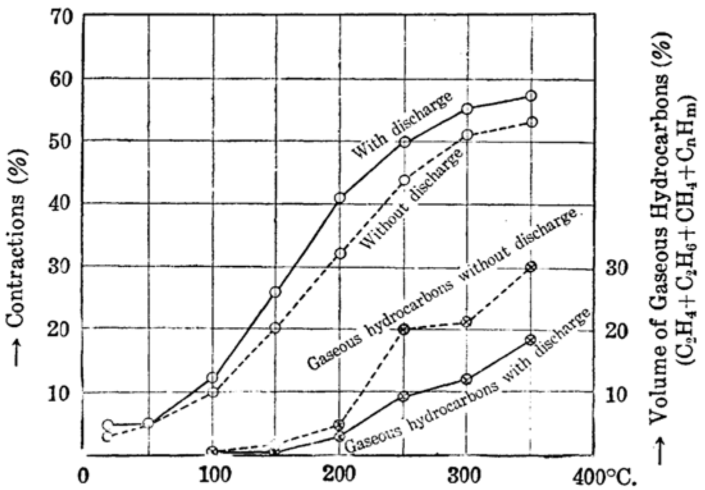

Fig. 6. Gas Contractions and the Volume of Gaseous Hydrocarbons with Ni-Catalyst.

contraction ratio is higher when high tension discharge is present at any temperature, but the difference is not so remarkable as in the case when the catalyst is absent. The effect of high tension discharge, however, is remarkably shown in the nature of the reaction, which is seen in the results of gas analysis. Namely, if we compare the total amount of gaseous hydrocarbons except acetylene ($C_2H_4+C_2H_6+CH_4+C_nH_m$) in both cases, we see that this amount is much smaller when discharge is present, which is also shown graphically in Fig. 6. This suggests that, when discharge is present, the reaction proceeds in the direction to form liquid

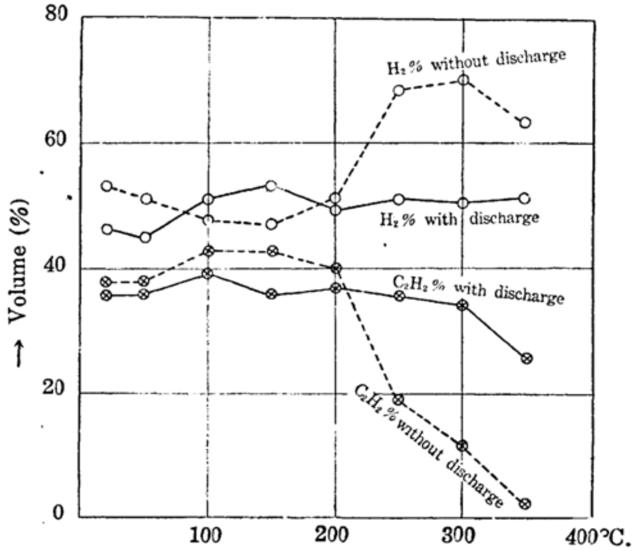

Fig. 7. Amount of H_2 and C_2H_2 in the Reacted Gases.

hydrocarbons, hydrogen being much consumed. Moreover, we see that, when discharge is present, the content of acetylene in the resulting gas does not change much as the temperature rises, while it decreases down to 2.5% when discharge is absent. As to the content of hydrogen, the matters are quite contrary, as is shown in Fig. 7. These facts, in connection with the above experimental results, suggest that when high tension discharge is absent, the main reaction is the polymerisation of acetylene, or if hydrogenation occurs, the products are mainly gaseous. On the contrary, when discharge is present, hydrogenation reaction occurs in connection with polymerisation, and the products are mainly liquid hydrocarbons. These results are as expected in the theoretical considerations. This method is favourable to produce liquid hydrocarbons from acetylene and hydrogen without producing gaseous hydrocarbons.

Summary.

(1) Some theoretical considerations with regard to the hydrogenation and polymerisation of acetylene have been made.

(2) The reaction has been studied in liquid phase with such catalysts as nickel, cobalt, palladium, and copper.

(3) The effect of high tension discharge has been studied with and without catalyst.

(4) It has been found that high tension discharge not only accelerates the reaction, but also changes the nature of the reaction.

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