The Synthesis of Iso- and Normal Butyl Alcohols in the Presence of Calcium Carbide. (B)* III.** Experimental Details and Preliminary Investigations on Methanol Catalysts in the Presence of the Carbide. Dry System.

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In our investigations on the non-catalytic polymerization of nascent acetylene, or the synthesis of liquid products directly from calcium carbide under ordinary⁽¹⁾ and elevated⁽²⁾ pressures, traces of alcohols have been detected in the liquid products. From the fact that methanol is the common intermediate in all the mechanisms, though they themselves differ widely; so far proposed for the formation of higher alcohols⁽³⁾ from carbon monoxide and hydrogen, the possibility of synthesizing higher alcohols, particularly the butanols*, in the presence of carbide, from the same gases passed over a methanol catalyst has been conceived.

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* R. Negishi, *Rev. Phys. Chem., Japan*, **15** (1941), 175; R. Negishi, *Rev. Phys. Chem., Japan* **15** (1941), 181 will be referred to as Papers (B) I and (B) II, respectively. (B) will be used to all the papers of this series in contradistinction to Papers I, II, etc., designated for the series of papers by the author on hydrocarbons from carbide, non-catalystic polymerization under ordinary and high pressures, and they will appear in *J. Chem. Soc. Ind., Japan.*

** This paper has been published by permission of Dr. S. Sato, the Director of the Central Laboratory, to whom the author's thanks are due.

(1) (a) R. Negishi, S. Kataoka, and O. Kamiike, *J. Soc. Chem. Ind. Japan*, **44** (1941), 1028; (b) O. Kamiike, S. Kataoka, M. Nibayashi, and R. Negishi, *ibid.* **44** (1941), 1030; (c–f) R. Negishi and O. Kamiike, *ibid.* **45** (1942), 133.

(2) (a) R. Negishi, M. Nibayashi, K. Sakon, and O. Kamiikè, *ibid.*, (1942); (b–c) R. Negishi, M. Nibayashi, and O. Kamiike, *ibid.*, (1942).

(3) See Paper (B) II.

* The author is grateful to Mr. O. Kamiike who has actually identified iso-butyl alcohol by distillation; its details will appear later in this Bulletin in a collaborated paper.

Considering further that the synthesis of higher alcohols is invariably associated with the formations of water and carbon dioxide molecules(4) and that the carbide has strong affinities for these molecules, its presence, therefore, would be of advantage. Moreover, thermodynamic calculations(5) have shown that the presence of the carbide increases the free energy of butanol formations to quite a degree. All these factors have encouraged us to take up the problem. There has been a further impetus for the investigation; it is a new method of synthesizing the butanols.

In this paper I shall limit myself to the discussion of the experimental procedure, the effects of dry carbide on the activity of the catalyst, and to the tabulation of a considerable body of the experimental results obtained*. Their fuller discussion will be published in this Bulletin later. The experimental details will be given rather minutely in order that the probable sources of error, difficulty, and the reliability of the results, not only in this paper but also in the entire series of our investigations, may be estimated.

Experimental Details. The same three revolving horizontal autoclaves of approximately one liter capacity, designated as I, II, and III(2a) were used. In later investigations an autoclave of entirely different design was employed.

In the dry systems investigated here, the carbide grains of 1 to 2 mm size and its acetylene content under the normal conditions of about 75 to 80% had been employed. The same gases as before(2a) were used. The methods of charging, discharging, and analysing the products had also been given before(2a). Gases and liquid products were analyzed, respectively, by a modified Schuftan's method(1b) (2a) and by elementary and distillation analyses.

Due to the limitations imposed upon the system by the construction of the autoclaves, it was not possible to maintain the total pressure of reaction at a constant value; so it was charged at the reaction temperature (or slightly lower, because the reaction is highly exothermic) to a predetermined value, and the gas was allowed to react until the pressure had decreased to a desired point. Then the gas was recharged to the original value. This was repeated as often as necessary until most of the carbide had reacted. Therefore, in all these runs it is not the reaction pressure but the reaction pressure range that is significant.

The volume of the charged gas was calculated from the blank determination made under the conditions as similar as possible to those of the actual runs. The volume of the gas after reaction was measured by means of a gas meter connected at the end of the condensing trains, which consisted of a water-cooling condenser and a trap cooled with solid CO_2-alcohol mixtures. The products condensed in the former was designated, as before, as "condenser" and those in the trap as "trap."

For these explorative and orientation runs, the liquid products were, as mentioned above. subjected to distillation, and the approximate alcoholic contents of the various fractions were determined. No special determinations of the hydrocarbons found in the fractions were made. In the more refined runs made later, the actual amount of iso-butyl alcohol was determined either by solvent analysis or by azeotropic distillation(6).

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(4) F. Fischer and H. Tropsch, *Die Umwandlung der Kohle in Oele*, **2** (1924), 246; P. K. Frolich and D. S. Cryder, *Ind. Eng. Chem.*, **22** (1930), 1051.

(5) R. Negishi, Paper (B) II.

* The author's thanks are due to Messrs. Sakon, Araki, Simono, and Kitakaze for making the autoclave runs; also to Messrs. Kataoka, Kodama, Nakano, and Inaba for analysing the products.

(6) R. Negishi and C. Isobe, this Bulletin, **16** (1941), 278.

Catalysts and their Preparation. The catalysts used in this series of runs, made in dry system, are designated as 15, 15b, 19, and 21. Their preparations will be briefly given. 15 and 15b were prepared under the same conditions by preparing 500 c.c. solutions containing 0.61 and 0.39 moles of chromium and zinc nitrates, respectively, and 150 g. of pumice grains of about 2 mm size was added to the mixture. The mixture was gradually dried at about 100°C; finally, it was calcined at 400°C in oxygen atmosphere for 4 and a half hours. Then it was reduced with H_2 at 400°C for 5 hours. The activities of these catalysts were not so good, but sufficient for our purpose. Catalysts 19 and 21 were prepared under the same conditions, employing a method similar to that of Molstad and Dodge(7). Solutions containing one mole per liter of chromium and zinc nitrates, both "Kojima" products, were mixed in the molal ratio of zinc to chromium as 0.39 to 0.61. It was then precipitated with an approximately 25% ammonium solution. Their activities were fair, but much more inferior to that given by the above investigators.

Table 1_A.

Elementary Analysis of Liquid Product.

Component	Liquid in Trap	Liquid in Condenser	Methanol
C	37·17	34.49	37.50
H	12.99	12.16	12.50
O*	49.84	53.35	50.00

* by difference.

Table 1_B.

Analysis of Gaseous Product.

Component	Gas	
	Initial	After Reaction
CO_2	3.3	6.4
C_nH_{2n}	0.0	0.0
O_2	0.5	0.4
CO	31.5	28.4
H_2	59.1	57.8
CH_4	0.0	0·8
N_2	5.6	6.1

The activities of 19 and 21 were found to be greater than those of 15 and 15b, though without significant effects on the character of the gaseous and liquid products. A more complete set of data for the latter catalysts is given below.

The activity of a catalyst is of second importance in our present case, since in the presence of the carbide, which has large affinities for water and carbon dioxide molecules: the equilibrium of the reaction is so greatly shifted, especially in a static system, by the continuous removal of the products. A catalyst with any activity has been found sufficient. However, the more active the catalyst is, the more rapidly the reaction comes to completion.

Effect on Activity of Carbide and of Reaction Products. The poisonous effects of carbide and of its reaction products on the activity of the catalyst do not seem to exist, as seen from Fig. 1, in which the results of run 97 (III$_A$Ser. 93) and of run 110_3 (III$_A$Ser. 100) are plotted together. In the former series 214 g. of catalyst 15 was used without carbide, and dp/dt, the rate of the total pressure change, of the last run of the series was plotted. In the latter series 212 g. of the same catalyst recovered after run 97 was mixed with 300 g. of the carbide, and dp/dt of one of the earlier runs in which the carbide had existed in excess and that of the last run, 110_3, of the series were plotted. In run 110_3 it might be assumed that no more carbide was present, as indicated by the absence of free acetylene when the residue was treated with water.

It is seen from the figure that the activity of the catalyst remains the same, within the accuracy of our measurements, even after 2500 minutes in contact with the

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(7) M. C. Molstad and B. F. Dodge, *Ind. Eng. Chem.*, **27** (1935), 134.

carbide and its reaction products. Though not given in this paper, the same sort of results has been shown in the other runs.*

Results. We shall now tabulate the results of our dry systems in the following Tables and describe each run briefly. The Table will be constantly referred to in a later paper in which a fuller discussion of the results is given. Of the runs listed, III_A Ser. 113 and III_A Ser. 100 are accurate enough for a quantitative discussion. Its detail will be given in one of the later papers. The conditions of the runs are given in Table 2.

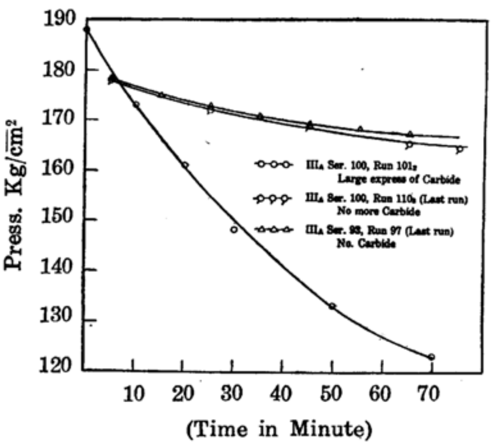

Fig. 1. Effect of Carbide on Activity of Catalyst XV.

Table 2. Experimental Conditions.

Exp. No.	Catalyst and Wt. (g.)	Carbide (g.)	$CO:H_2$	React. Temp. (°C.)	Press. Range Kg/cm².
III_A 111 ……..	216.5(15b)	0	1:1.88	320	203
III_A Ser. 100 ….	212 (15)	300	1:1.89	320	183–175
III_A Ser. 135** ..	119·2(15)	200	1:1.89	320	130– 90
III_A Ser. 113 ….	216 (15b)	300	1:1.85	280–320	165–135
IV_A Ser. 52 …..	100(19+21)	500	1:2	305	200–100

* Autoclave II was used in every case. Catalyst was mixed with carbide.
** Catalyst placed "in cylinder," was supported at the center of the autoclave.

Run III_A 111. The purpose of this run was to see what would be formed from the catalyst. As mentioned already, it produced mainly methanol.

Run III_A Ser. 100 (runs 100 to 110). In every run two charges of gas were made to maintain a given range of pressure, and one complete discharge was made. For the last run, 110_3, three charges were made, because the reaction was quite slow, especially under the lower pressure. Each run required from 240 to 400 minutes. The total time of reaction was about 60 hours. The results of this run were quantitative and would be discussed in a later paper.

Run III_A Ser. 113 (runs 113 to 134). In this series the reaction temperature had been varied from 280 to 320°C., but most of the runs were made at 295 to 305°C. For the slower reactions a discharge was made for each charging, but, when the reactions were rapid (above 300°C.), two charges were made for each discharge. The total time of

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* The longest run we have made is not over 150 hours.

reaction was 84 hours. These results were quantitative and would be discussed in a later paper.

Run III_A *Ser. 135 (run 135 to 137)*. The catalyst was charged "in cylinder", and supported in the center of the autoclave. The purpose of this run was to investigate the effect of the catalyst not in contact with the carbide. From the results of the elementary analysis of the liquids and from the gas analysis, shown in Tables 3 and 4, respectively, it is obvious that the differences are small, but they are probably real. The fact that in III_A Ser. 100 there is less oxygen in the liquid products and more saturated gases seems to point to the same conclusion that the actual temperature in III_A Ser. 100 is higher than that of III_A Ser. 135. Similar evidence has been obtained in our synthesis of hydrocarbons directly from the carbide under the elevated pressure (2b, c).

Table 3. Elementary Analysis of Liquid Products.

Exp. No.	Liquids in the Condenser			Liquids in the Trap		
	C	H	O	C	H	O
Methanol	37.50	12.50	50.00	——	——	——
III_A 111	34.49	12.16	53.35	37.17	12.99	49.84
III_A Ser. 100	77.90	11.69	10.41	66.80	12.58	20.72
III_A Ser. 135	74.35	12.24	13.42	64.15	12.91	22.94
III_A Ser. 113	72.46	11.69	15.85	55.64	15.00	29.36
IV_A Ser. 52	75.49	11.73	12.78	70.51	12.60	16.89
Isobutanol	64.86	13.51	21.62	——	——	——

Run IV_A *Ser. 52 (run 52 to 67)*. The reaction temperature was varied from 290 to 305°C., but most of the runs were made at 300 to 305°C. The purpose of this run was to investigate the effect of excessive carbide. Two pronounced effects were observed. One of them was a reduced oxygen content in the liquid products. This was ascribed as due to excessive dehydration by the carbide. It seemed that even some of the butyl alcohol synthesized from the methanol was dehydrated with a subsequent polymerization of the resulting unsaturated substances to form the hydrocarbon liquids with reduced oxygen content. The second effect was associated with the sudden increases, which we had designated as "jumps",(1),(2) in both pressure and temperature. We are at a loss for a suitable explanation of this phenomenon. It was generally found that the apparent value of dp/dt reached a maximum only after a considerable amount of the carbide had reacted, and the rate again decreased until it finally reached that of the original value. Perhaps, the jumps are associated with this, but, as has been mentioned above, we are in the dark with regard to this phenomenon. These jumps also took place in Run III_A Ser. 40, in which 500 g. of the carbide was used. No jump had occurred when 300 g. or less of carbide was taken although the existence of a maximum in dp/dt was evident.

Table 4. Gas Analysis.

Exp. No. Auto. Run	III_A 135				IV_A 52**				III_A 113***					III_A 111		III_A 100□		
Run	135		136		57		59	64	115	124		128		111		100□□	104	
Gas ↓	Orig.	React	React	Trap*	React	Trap	React	"Jump"	React	React	Trap	React	Trap.	Orig.	React	React	React	Trap
CO_2	3.2	0.0	0.0	1.5	0.2	58.1	0·4	0.0	0.2	0.0	24.5	0.0	20.7	3.3	5·5	0.0	0.0	62.0
C_2H_2	0.0	0.0	0.0	10.5	0.5	24.8	0.4	0.0	1.1	0.5	66.0	0.7	70.4	0.0	0.9	2.0	0.2	16.8
C_2H_4	0.0	1.4	2.5	14·0	3.6	11.1	3.2	0.7	0.5	0·9	5.6	1.3	5.2	0.0	0.0	1.0	1.8	10.8
C_nH_{2n}	0.0	2.0	1.5	1.0	1.3	0.6	0.9	0.0	1.6	1.6	0.7	2.2	0.7	0.0	0.0	1.6	3.0	0.7
O_2	0.5	0.6	0.5	0.5	0.5	0.0	0·5	0.7	0.7	0.5	0.5	0.4	0.4	0.5	0.5	0.7	0.5	0.3
CO	31.3	29.7	28.5	6.1	29.5	0.2	29.8	1.3	31.0	28.5	0.8	25.6	0.7	31.5	28.1	24.5	20.2	0.7
H_2	59.2	54.3	55.9	1·5	61.3	0.2	52.3	11.0	57.3	58·2	0.0	58.4	0.0	59.1	27.8	50.8	53.3	0.9
CH_4	0.3	3.3	2.9	2.8	0.0	0.0	9.7	71.2	0.5	0.7	0.0	2.1	0.0	0.0	0.8	7.6	9.0	0.0
C_2H_6	0.0	1.7	1.7	17.1	0·0	2.2	0.0	11.5	0.5	2.3	0.0	1.2	0.0	0.0	0·0	3.9	5.2	5.0
C_3H_8	—	—	—	—	—	2.5	—	—	—	—	—	—	—	—	—	—	—	1.0
N_2	6.8	7.0	6.5	37.1	3.1	0.3	2.8	3.5	6.6	6.8	2.7	8.1	1.9	5.6	6.1	7·9	6.8	1.8
Reaction Temp. °C	320				305			496	290			306		320		320		

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* Unreliable; probably air was mixed.

** Runs 57, 59, and 64 are the 5th, 6th and 10th runs of the series (of 13 runs); Press. of jump was above 300 Kg/cm^2 (off scale).

*** 124 and 128 are the 12th and 16th runs of the series (of 22 runs); 115 is the 3rd.

□ 100 and 104 are, respectively, the 1st and 5th runs of the series (11 runs).

□□ The same gas as that of III_A 111 was used.

Some of the results of the gas analysis are shown in Table 4. Others were omitted simply because most of the results of the same series varied only slightly from run to run. Only what seems to be more or less typical has been given. Several interesting facts can be pointed out from the Table. The high content of saturated gases in run 64 is obviously associated with the jumps nearly 200°C. in temperature and at least 150 Kg/cm^2 in pressure. Also in the same series, the results of runs 57 and 59, which have been made successively, show interesting effects for which no suitable explanation is found. In the former, and up to this run, there is no formation of saturated gases; but in 59, which has been made under about the same conditions as those of the former, there appears suddenly a rather large quantity of methane. Moreover, the methane formation of approximately this extent has been observed throughout the rest of the runs of the series. No such effect has been found with the other series; not even in III$_A$ Ser. 40, which has been carried out at 310°C. The results of Table 4 will be referred to again in the next paper when a discussion of the results of gas analysis of the runs made in liquid medium is taken up.

NOTE. Most of the results given in this paper and in the following (IV and V) were completed in 1939–1940, but the publication of them has been with-held.

Summary.

The experimental procedure and the preparations of the catalysts used are given in detail. The effects on the activity of the carbide and of the reaction products are found to be small—if at all.

The results of the runs in dry system are tabulated, and each run is briefly described. Short discussions on the results are also given. A fuller discussion on them is reserved for a subsequent paper.

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