The Synthesis of Iso- and Normal Butyl Alcohols in the Presence of Calcium Carbide (B) IV*. Synthesis in Liquid Paraffin. Static System.

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It has been shown in one of my papers that a large amount of heat is evolved when calcium carbide reacts(1). In dry system the localization and accumulation of heat result, augmenting unfavourable side reactions.

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[*] This paper will appear in Japanese in *Rev. Phys. Chem. Japan*, **16**(1942).

(1) Under certain tolerable assumptions, the heat of reaction evolved at 310°C for autoclave run III_A Ser. 113 has been calculated to be about 114 kcal./mole of 70% carbide reacted.

In order to mitigate these effects, I have attempted to carry out the synthesis of butanols in the presence of calcium carbide in a liquid medium, and the results obtained are presented here. A comparison of these results and those of the dry systems(2) will be given in my next paper, and here, I shall be concerned more with the gaseous products.

Experimental Details(3). (1) *Method.* The same one-liter revolving autoclave used in the dry systems was again employed. A mixture of carbide and catalyst, both of 60 mesh powders, was charged; liquid paraffin was then added, and the components were mixed. The air in the autoclave was flushed out several times with the reaction gas (or hydrogen), and the temperature was raised to a desired point. The reaction gas was then charged and recharged as often as necessary to maintain the pressure range within the proper limits. Usually, two or three chargings, at or at slightly lower than the reaction temperature, were made for each discharge. Except for the final discharge of the final run of a series, the products were discharged to two or three atmospheres in order to prevent, to a maximum degree, a loss of the medium. The products were condensed as before(2).

(2) **Materials.** (a) *Carbide.* Its final acetylene content, under the standard conditions, was from 70 to 75%. A typical analysis showed:

Subst.	CaC_2	CaO	SiO_2	Al_2O_3	Fe_2O_3	Others*
Weight (%)	72	14.5	3.5	2.4	0.6	7.1

* They contained $CaCO_3$ and some sulphur and phosphorus compounds.

(b) *Liquid Paraffin.* A commercial product was distilled under 5 mm Hg pressure in CO_2 atmosphere(1), and all the light boiling substances, which distilled out when the liquid temperature in the flask was maintained constant at 250°C, were eliminated. Under the standard conditions, the temperature of the liquid corresponded to 430°C, and the maximum vapour temperature attained was 410°C. The whole apparatus was of Terex glass. The elementary analysis of the liquid, designated as Paraffin Oil III, showed:

$$C=85.55,\ H=14.08,\ O=0.37\ \text{(by difference)}.$$

(c) *Gases.* Water gas was prepared by a technical method. It was used without purification. Hydrogen was a commercial product of about 98% purity. No purification was effected.

(d) *Catalysts.* The catalyst used are given in Table 1. Their preparations were the same as those given in Paper (B) III(2).

Some effects on the catalytic activity of thorium will be mentioned briefly. As Fig. 1 indicates, a small concentration of thorium increases the total yield, and there is an optimum content which lies in the range,

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(2) R. Negishi, Paper (B) III, this Bulletin, **17**(1942), 179.

(3) The writer is grateful to Messrs. Sakon, Araki, Simono, and Kano for their experimental assistance.

Table 1.

Methanol Catalysts, their Composition.

(Reduced with H_2 at 400°C. for 4 hours.)

Catalyst No.	Composition in Mole Ratio	Precipitating Agent	Activity*
18ab	Zn : Cr : Th 1 : 1 : 0.05	6 molal K_2CO_3	Good
21	Zn : Cr 39 : 61	25% NH_3	Fair
36a	Zn : Cr : Th 1 : 1 : 0.2	40% K_2CO_3	Good
25	Zn : Cr 39 : 61	28% NH_3	Fair

* Relative, based on the total liquid products, including water, and higher boiling substances.

0.05 to 0.20 moles(4). The effect on the character of the products of thorium seems but slight, as may be seen from the results given in Table 2.

Autoclave runs VIII_A Ser. 6 and VIII_A Ser. 11 were made, respectively, in the closed autoclaves II and III and both runs extended over 40 hours in 15 days. II_{CA} Ser. 68 was made with a catalyst in pellets (50 g. of which occupied about 40 c.c.), packed in a reaction tube of 2.5 cm. diameter and with space velocities varying rom 3000 to 13500; the reaction period was 95 hours, extending over 12 days.

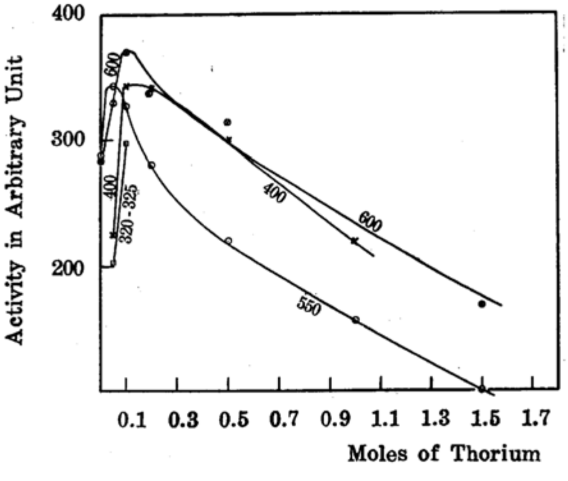

Fig. 1. Activity vs. Thorium Content (Temp. °C. of Reduction Indicated in Fig.)

We shall continue to investigate the effect of thorium and soon we may be able to state with more assurance the real effect of it. At this stage of progress, however, we can merely say that a small amount of thorium seems beneficial, as far as the total yield(5), but not necessarily methanol, is concerned.

(3) *Analysis*(6). Gaseous, liquid, and solid products were analysed as before(7)(8). The solid residue was separated from the medium by washing with ether and filtering under vacuum. The amount of the medium was then determined by evaporating off the ether under reduced pressure. The acetylene and carbo-

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(4) No effect of the temperature of reduction has been taken into account, but it is evident in the Fig.

(5) This is important, since in our case, not only the formation of the butanols but also that of hydrocarbons, as by-products, is not undesirable.

(6) The writer's thanks are due to Mr. O. Kamiike and to his assistants.

(7) O. Kamiike, S. Kataoka, M. Nibayashi, and R. Negishi, *J. Soc. Chem. Ind., Japan*, **44** (1941), 1030.

(8) R. Negishi, M. Nibayashi, K. Sakon, and O. Kamiike, *ibid.*, (1942), 366.

Table 2. Methanol from Various Catalysts.

(Water gas used without purification; $CO:H_2$ about 1:1.25)

Exp. No.	Catalyst No. and Composition*	Vol. Methanol*** (%)	Vol. Other Prods.** (%)	Reaction Conds.	
				Temp. (°C.)	Press. Kg./cm^2.
Auto. VIII$_A$ Ser. 6	66, Cr : Zn 1 : 1	88.5	2.7	320	200–170
Auto. VIII$_A$ Ser. 11	67, Cr : Zn : Th 1 : 1 : 0.1	86	3.5	320	200–170
II$_{CA}$ Ser. 68 (68–86)****	II$_{CA}$ Cr : Zn : Th 0.4 : 0.6 : 0.05	85-88	10	330	200

* Mole ratio.

** Consist mostly of water and hydrocarbons; distillation losses not included.

*** Based on total liquid products.

**** Runs 68 and 69 not included. These runs were made at space velocities of 1000 and 2000, respectively. Their methanol vol. % was about 81, much less than the others made at higher space velocities (3000–13500).

nate contents of the residue were determined by taking average results of a large number of samples of the residue mixture, as discharged (including the medium), which were treated with warm water alone and with phosphoric acid, respectively. Blank tests have shown that this method is not reliable more than to 5% which is, however, sufficient for our present purpose. Lack of accuracy is partially compensated by the simplicity of the method.

Results and Discussion. The experimental conditions and some of the results obtained in the liquid system are shown in Tables 3, 4, 5, and 6. In agreement with what has been found(1) at 330°C but a slight amount of the medium is cracked, as shown in Table 3. It is rather startling that so much condensates have been obtained in the condenser, even at 300°C, in the presence of the carbide. A plausible explanation of this seems that a part of the medium has been forced out rather than cracked and distilled out. This has been definitely the case with runs 82 and 98. There is a trend in the amounts of condenser condensates with the reaction temperatures, but there may be no real significance in this parallelism. However, there is no reason to doubt that the presence of the carbide increases cracking of the medium(1), as seen from the results of IV$_A$ Ser. 139 and IV$_A$ Ser. 124(9). In the latter run there is 41.7 c.c. of the fractions boiling lower than the original, as compared with only 6.7 c.c. in the former in which no carbide is present.

The results of Table 4 indicate that the lower the reaction temperature, the larger is the amount of the fraction boiling below 230°C. The same sort of relationship exists between the yield of iso-butyl alcohol and the temperature, as seen from Table 5. With decreasing temperature, however, the rate of reaction becomes quite slow.

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(9) The results of this series are sufficiently reliable, and their quantitative discussion will be reserved for the next paper to be published in this Bulletin.

Table 6 gives the summarized results of gas analysis. There is no trend in the formations of the gases, except for methane, with temperature. It is of some interest to note that, as in all our carbide reactions, large amounts of ethylene, propane, and butane are present in the condensable gases (the gases condensed and dissolved in a trap cooled with

Table 3. Experimental Conditions.

Exp. No.*	Ser. 178	Ser. 139	Ser. 124	Ser. 58	Ser. 82	Ser. 98
Autoclave Used	II	II	II	III	III	II
CO:H_2	1:1.23	1:1.35	1:1.3	1:2	1:1.75	1:1.7
Catalyst No. and Wt (g.)	36a, 45	None	18ab, 45	21, 22	21, 30	25, 30
Carbide (g.)	300	None	300	220	300	301
Paraffin (g.)	300	303	300	220	301	300
Temp. (°C.)	300	330***	330	350	360	340-365
Press. Range Kg./cm^2.	200-150	200	200-160	198-130	200–120	200–120
Time (Min.)	1870	1995	2220	1840	1840	2145
Condensates Cond. c.c.	26	2.6	52.2	94.4‡	253.2‡	258.6‡
g.	—	2.1	40.4	73.6	205.9	208.7
Trap. c.c.	21.1	0	35.4	37.4	31.4	19.0
g.	17.7	0	24	25 5	19.5	12.8
Paraffin in the Residue (g.)	—	292	288	160	102	85
Liquid boiling below Original (c.c.)	—	6.7	41.7	6.7	—	—
Condensed and Dissolved Gas** (g.)	2 3	—	15.7	26.5	11.5	8.0

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* Autoclave run series IV$_A$ tabulated; Paraffin Oil III used.

** Condensed and dissolved gas found in the trap, cooled with alcohol and solid CO_2, connected to the autoclave.

*** The first 150 minutes at 350°C.

‡ Probably due to forcing out of the medium.

Table 4. Distillation Analysis* (Vol. %).

Temp. Range (°C.)	IV$_A$ Ser. 124	IV$_A$ Ser. 178	IV$_A$ Ser. 82
<100	18.8	11.5	2.5
100–150	35.4	43.5	13.7
150–230	27.6	29.0	25.0
230–270	Began to crack at 216°C	—	13.4
270–300	—	—	12.2
Residue	10.8	—	24.0
Loss	7.4	—	9.2

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* Made by Mr. O. Kamiike. The author takes this occasion to thank him for his co-operation.

Table 5. Effect on the Yield of Iso-butanol of Temperature.

Exp. No.	Vol. of Crude Isobutanol* (103–110°C.) (%)	Reaction Temp. (°C.)
IV$_A$ Ser. 178	18	300–305
IV$_A$ Ser. 124	16	330
IV$_A$ Ser. 82	1.8	360

* Based on the total liquid condensates, exclusively of the condensates found in the trap.

Table 6. Gas Analysis*, **.

Temp. (°C.) and Exp. No.	300 178	330 139***	330 124	340 98	350 58 React.	 Trap.	360 82 React.	 Trap.
CO_2	0.2	3.3	0.0	0.3	0.0	29.8	0.3	4.2
C_2H_2	1.5	0.0	0.7	0.7	0.0	18.9	0.6	6.8
C_2H_4	3.0	0.3	1.2	1.0	3.0	17.3	1.7	22.0
C_nH_{2n}	0.8	0.0	1.1	0.2	0.3	0.0	0.4	3.0
O_2	0.4	0.4	0.3	0.5	0.5	0.0	0.9	0.4
CO	40.1	38.0	40.7	30.8	26.9	0.0	28.1	0.5
H_2	47.5	33.4	50.0	55.5	50.6	0.0	27.8	0.0
CH_4	3.7	2.1	4.3	6.5	15.4	0.0	34.1	0.0
N_2	2.8	2.5	1.7	3.5	2.3	0.0	6.1	1.8
C_3H_8	—	—	—	—	—	14.6	—	13.8
C_4H_{10}	—	—	—	—	—	18.7	—	47.1
Run No.	185	142	131	98	73		89	

* Since CO:H_2 varied for different runs, comparison cannot be quantitative.
** Approximately the middle run of each series taken.
*** No carbide is present.

alcohol and solid carbon dioxide). The presence of ethylene may be qualitatively accounted for by the results of Taylor and Van Hook(10) or of Farkas and Farkas(11) that the hydrogenation of acetylene to form ethylene is quite rapid and complete. The formations of butane and propane may be explained by the consideration of Egloff(12) that ethylene is the key molecule for the synthesis of hydrocarbons. He assigns to the reaction, $2CH_2=CH_2 \rightarrow CH_3CH_2CH=CH_2$, which takes place quite readily according to various investigators(10)(12)(13), the activation energy of 35–37.7 kcal. per mole. In a closed system here employed, with excess of hydrogen, it is conceivable that the butylene thus formed is hydrogenated to butane. To account for the formation of propane, we shall

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(10) H. A. Taylor and A. Van Hook, *J. Phys. Chem.*, **39** (1935), 811.

(11) A. Farkas and L. Farkas, *J. Am. Chem. Soc.*, **61** (1939), 3396. According to them, the activation energy is 12–17 kcal. on platinum surface, and according to Ref. (5), it is about 42 kcal./mol. in gas reaction.

(12) G. Egloff and E. Wilson, *Ind. Eng. Chem.*, **27** (1935), 917.

(13) Storch, *J. Am. Chem. Soc.*, **56** (1934), 374.

seek an additional explanation in the results of Storch(13) in which ethylene has been polymerized at 377°C and 141.5 mm. For the contact times less than 2 hours the formation of butene predominates, but for 3 hours that of propene becomes largest. He has explained the presence of the olefines with odd number of carbon atoms by assuming a disproportionation to give a higher and a lower olefine, taking one of his examples,

$$C_2H_4 + C_4H_8 \begin{array}{l} \nearrow 2\,C_3H_6 \\ \searrow C_6H_{12} \end{array} .$$

It seems reasonable that this propene(14) is then hydrogenated to propane in our case.

The question as to whether ethane is present or not in these experiments made in liquid medium is, from our available data, not possible to be answered.

In our gas analysis the components of the saturated gases in a mixture have been calculated from the volume decrease and the volume of carbon dioxide produced after explosion. If the mixture contains more than two components, there will be a freedom of choice of any two components from the lot. This introduces uncertainty, as seems to be indicated by the results of the analysis of the gases found in the trap of IV_A Ser. 124 shown in Table 6B. Though there is this shortcoming in the method of analysis, it seems quite unlikely that it is a matter of chance that no ethane (or very slight) is found in the results of all the runs made in liquid medium while there is abundance of it in dry.

Table 6B. Analysis of Trap Gases for Autoclave Run IV_A Ser. 124.

Run No. Gas	130	133	135
CO_2	26.1	30.2	32.1
C_2H_2	12.9	16.2	18.2
C_2H_4	30.4	24.8	37.1
C_nH_{2n}	1.5	1.3	1.2
O_2	0.0	0.2	0.0
CO	3.1	2.8	0.8
H_2	0.0	0.8	0.3
CH_4	11.3	8.2	0.0
C_2H_6	14.6	14.4	0.0
C_3H_8	0.0	0.0	10.3

From theoretical considerations, however, the absence of ethane in excess of ethylene and hydrogen may not be entirely out of order. The following considerations are suggestive in this connection.

First, according to the work of Wood (quoted from Egloff(12)), the temperature for the initial appearance and the maximum formation of products in the thermal reactions of ethylene are as shown in Table 7.

Second, according to the results of Moore and Taylor(15), in their work on the mercury photosensitized hydrogenation of olefines, with about 40 mm. of olefine plus six fold excess of hydrogen, there is a significantly

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(14) According to Ellis, "The Chemistry of Petroleum Derivatives," Vol. I, 80, The Chem. Catalog Co., Inc., N. Y., 1934, the results of Schneider and Frolich and of Lenher indicate that reactions of the type, $3C_2H_4=2C_3H_6$, e.g., the transformation of ethylene to propylene and not to butylene, can also take place although the mechanism of such reactions is still very obscure.

(15) W. J. Moore, Jr. and H. S. Taylor, *J. Chem. Phys.*, **8**(1940), 504.

Table 7.

Products	Temperature (°C.)	
	Initial Appearance	Maximum Formation
C_4H_8, C_4H_6	350–400	650–750
C_2H_6	450–500	700
CH_4	500	1000
C_2H_2	650–700	1400
Aromatics	650	800–850

greater formation of propane and of butane from the respective olefines than that of ethane from ethylene. Their table is reproduced in Table 8.

Third, from the consideration of the energy of activation, it is of interest to note that the energy of activation of ethylene polymerization is less than that of hydrogenation, 35–37.7 kcal./mole as against 43.2 to 51.5 kcal./mole⁽¹²⁾ for the latter. Among ethylene, propylene, and butylene, the magnitude of the energy of activation of hydrogenation decreases with increasing molecular weight, as seen from the results obtained by Twigg⁽¹⁶⁾ on the exchange and hydrogenation reactions between deuterium and the olefines on reduced nickel at 55–120°C. His results are given in Table 9. Toyama⁽¹⁷⁾ and Kiyama⁽¹⁸⁾ obtained a similar relative order of the activation energies of hydrogenation for the hydrogenation of ethylene, propylene, and isobutene also on reduced nickel at about the same temperature range.

Table 8.

Olefine Used	Olefine to Saturated Products (%)						
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_8H_{18}
C_2H_4	2	14	—	84	—	—	—
C_3H_6	2	1	26	5	2	64	—
C_4H_8	3	1	1	29	—	—	66

Table 9.

Olefine	Activation Energy kcal./Mol.
Ethylene	8.2±0.5
Propylene	6.0
Butene-2	3.3
Isobutene	3.3

From what has been mentioned above, the absence of ethane in our experiments may not be out of harmony with the experimental facts already existing; but these considerations do not still completely explain why ethane is present in dry system while not in liquid medium⁽¹⁹⁾.

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(16) G. H. Twigg, *Trans. Faraday Soc.*, **35**(1939), 934.

(17) O. Toyama, *Rev. Phys. Chem. Japan*, **11**(1937), 353; **12**(1938), 115; **14**(1940), 86.

(18) R. Kiyama, *Rev. Phys. Chem. Japan*, **15**(1941), 137.

(19) Localization and accumulation of the heat of reaction in dry system may be the cause, but in lack of more definite evidence, this argument should not be pushed too strongly. The difference in the rates of polymerization in the two systems may not be entirely neglected from consideration.

Summary.

The synthesis of isobutyl alcohol in the presence of calcium carbide and a methanol catalyst has been made in liquid paraffin. It has been found that the reaction proceeds more smoothly, though not necessarily more effectively, than in dry system.

The effect of thorium on the catalytic activity of methanol catalyst has been investigated briefly. It has been found that 0.05 to 0.2 mole of it will increase the total yield of liquid products, but will not affect appreciably that of methanol.

The preponderate formations of ethylene, propane, and butane and the absence of ethane, even in the presence of excess ethylene and hyrogen, have been qualitatively explained.

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