THE SYNTHESIS OF ISO- AND NORMAL BUTYL ALCOHOLS IN THE PRESENCE OF CALCIUM CARBIDE.[*, 1]

By R. NEGISHI.

In one of my previous papers[2] I have shown, in a general manner, that many organic substances can be directly synthesized from calcium carbide. It is now my intention in this paper to show whether or not this new method of synthesis can be controlled, to some extent, to produce butyl alcohols (limited to iso- and normal). I have chosen this synthesis, because there has been evidence that some alcohols can be formed when the carbide is reacted both under ordinary[3] and under elevated pressures[4], and because of its interest, academically and practically, as a source of the butenes which can be readily transformed into aviation gasoline and ingredients of high octane number. This synthesis has proved not only, heretofore, unreported in the literature, but it also takes place quite satisfactorily under practical conditions, and the experimental results** are predictable from the theory.

Before discussing the experimental data, which have definite bearing on the subject, some thermodynamic calculations on the free energies of the syntheses will be made. They will be given in the Tables and Fig. 1 below. For these calculations the same notations, relations, and equations for the standard free energy of formation as those given in one of my papers[2], which will be henceforth designated as Paper (A) I, have been used. For the sake of convenience, the equations for those substances here involved will be given again in Table I.

In Table II ΔF°, the standard free energy of formation, at 100, 300, and 500°C, calculated from the equations in Table I are shown, and in Table III ΔF, the free energy of reaction involving the formation of one mole of iso- or normal

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[*] It is the writer's pleasure to thank Dr. M. Sato for the permission for publication.

[1] R. Negishi, This Journal, **15**, 127 (1941).

[2] R. Negishi, O. Kimura, and O. Kamiike, This Journal, **15**, 31 (1941). This paper will henceforth be referred to as Paper (A) I.

[3] R. Negishi and O. Kamiike, Papers I—VI, a series of papers on the direct synthesis of hydrocarbons from the carbide under ordinary pressure, to appear in *J. Soc. Chem. Ind., Japan*, (1941).

[4] R. Negishi, M. Nibayashi, and O. Kamiike, Papers I—III, a series of papers on the direct synthesis of hydrocarbons from the carbide under elevated pressure, to appear in *J. Soc. Chem Ind., Japan*, (1942).

[**] They will be described fully in *J. Chem. Soc., Japan*, (1942). The writer is grateful to Messrs. Sakon, Araki, Simono, and Kano for making the autoclave runs; also to his colleagues, Dr. S. Hamai, Messrs. Kamiike, Nibayashi, Isobe, and Kataoka for their hearty cooperation throughout this work.

Table I.

The Standard Free Energy of Formation.*

Substance	Equation	Reference
CO	$-27070-2.05\,T\ln T+0.00225\,T^2-0.20\,(10^{-6})\,T^3-7.92\,T$	7
CO_2	$-94210+0.30\,T\ln T-0.0003\,T^2+0.05\,(10^{-6})\,T^3-0.94\,T$	7
C_2H_2	$+54882-13.56\,T$	2
CH_3OH	$-47130+17.29\,T\ln T-0.014\,T^2-82\,T$	6
C_2H_5OH	$-50520+20.33\,T\ln T-0.0131\,T^2-85\,T$	6
n-C_4H_9OH	$-59470+26.41\,T\ln T-0.0113\,T^2-86.8\,T$	6
iso-C_4H_9OH	$-60020+28.77\,T\ln T-0.0106\,T^2-106.16\,T$	6
H_2O	$-57120+2.75\,T\ln T-0.00075\,T^2-6.65\,T$	7
Carbide	$-13210+6.9\,T\ln T-31.47\,T$	8
CaO	$-152640-2.25\,T\ln T-0.0015\,T^2+37.53\,T$	2
$CaCO_3$(calcite)	$-290334+0.723\,T\ln T-2.778\,(10^{-3})\,T^2-3.13\,(10^{-6})\,T^3+95350/T+61.30\,T$	2
n-C_4H_8	$-1897+62.67\,T$	5
iso-C_4H_8	$-4540+63.02\,T$	2
n-C_4H_{10}	$-32292+91.58\,T$	2

* As in Paper (A) I, these equations are not necessarily the most accurate ones. The same equations have been used for the sake of comparison. For the more accurate or recent thermodynamic data see:

K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940); *J. Am. Chem. Soc.*, **62**, 1224 (1940); *Chem. Rev.*, **27**, 39 (1940); F. D. Rossini, *J. Research Natl. Bur. Stds.*, **22**, 407 (1939); *Chem. Rev.*, **27**, 1 (1940); G. S. Parks, *ibid.*, **27**, 75 (1940); C. M. Thacker, H. O. Folkins, and E. L. Miller, *Ind. Eng. Chem.*, **33**, 584 (1941); K. Kawakita, This Journal, **15**, 118 (1941), (Review In Japanese).

Table II.

The Standard Free Energy of Formation, F°.

Substance	100° C	300° C	500° C
CO	−34200	−38400	−42500
CO_2	−93900	−93700	−93500
C_2H_2	49800	47100	44400
n-C_4H_8	21500	34000	46600
iso-C_2H_8	19000	31600	44200
n-C_4H_{10}	1880	20200	38500
CH_3OH	−41500	−35900	−30100
C_2H_5OH	−39200	−29600	−19700
n-C_4H_9OH	−35100	−16900	2300
iso-C_4H_9OH	−37600	−19700	−680
H_2O	−53600	−51200	−48600
CaC_2	−18300	−20300	−22100
CaO	−143800	−139800	−136100
$CaCO_3$	−266200	−253900	−242200

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5) Calculated as in Paper (A) I from the data given by C. L. Thomas, G. Egloff, and J C. Morrell, *Ind. Eng. Chem.*, **29**, 1260 (1937).

6) A. W. Francis, *ibid.*, **20**, 283 (1928).

7) J. Chipman, *ibid.*, **24**, 1013 (1932).

8) K. K. Kelley, *Bur. Mines*, Bull. No. 407, 8 (1937).

Table III.

Reaction	ΔF		
	100°C	300°C	500°C
1) From Element			
1a $4C+5H_2+1/2O_2=iso\text{-}C_4H_9OH$	−37600	−19700	−700
1b $4C+5H_2+1/2O_2=n\text{-}C_4H_9OH$	−35100	−16900	+2300
2) From Acetylene			
$2C_2H_2+H_2O+2H_2=iso\text{-}C_4H_9OH$	−83600	−62800	−40900
3) From Carbide+Water			
$2CaC_2+3H_2O+2H_2=iso\text{-}C_4H_9OH+2CaO$	−127700	−105100	−82800
4) From Olefins⁹⁾			
4a $n\text{-}C_4H_8+H_2O=n\text{-}C_4H_9OH$	−3000	+250	+4300
4b $iso\text{-}C_4H_8+H_2O=iso\text{-}C_4H_9OH$	−2900	−140	+3700
5) From Water-gas			
$4CO+8H_2=iso\text{-}C_4H_9OH+3H_2O$	−51500	−19800	+13400
6) From Water-gas+Carbide+CO_2*			
$4CO+8H_2+3CaC_2+3CO_2=iso\text{-}C_4H_6OH+3C_2H_2+3CaCO_3$ $\lfloor$Polymerize $\rightarrow$	−212800	−144400	−77200
7) From CO_2+Methyl alcohol+Oxygen¹⁰⁾			
$8H_2+2CO_2+2CH_3OH+O_2=iso\text{-}C_4H_9OH+7H_2O$	−142200	−118600	−93500
8) From Ethyl Alcohol¹¹⁾			
$2C_2H_5OH=n\text{-}C_4H_9OH+H_2O$	−10400	−8800	−7000
9) From Ethyl Alcohol+Carbide†			
$2C_2H_5OH+CaC_2+CO_2=n\text{-}C_4H_9OH+C_2H_2+CaCO_3$ $\lfloor$Polymerize $\rightarrow$	−60800	−50400	−40500
10) From Methyl and Ethyl Alcohols¹²⁾			
$2CH_3OH+C_2H_5OH=iso\text{-}C_4H_9OH+2H_2O$	−22700	−20700	−18000
11) From Methyl and Ethyl Alcohols+Carbide‡			
$2CH_3OH+C_2H_5OH+2CaC_2+2CO_2=iso\text{-}C_4H_9OH+2C_2H_2+2CaCO_3$ $\lfloor$Polymerize $\rightarrow$	−123500	−103800	−85100
12) Oxidation of Butane¹³⁾			
$C_4H_{10}+1/2O_2=C_4H_9OH$	−39500	−39900	−39300
13) From CO_2 and $H_2$¹⁴⁾			
$2CO_2+4H_2=CH_3OH+CO+H_2O$	+4800	+10900	+17400

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9) R. Fussteig, *Petroleum Z.*, 33, 4 (1937). In this work the production of pure ethyl, butyl, and $C_5H_{11}OH$ by selective absorption of the corresponding olefins in the appropriate concentration of H_2SO_4 with AgCl as catalyst is given. Also G. Egloff, "Reactions of Pure Hydrocarbons," Reinhold Publish. Corp., N. Y. (1937); C. Ellis, "The Chemistry of Petroleum Derivative," Reinhold Publish. Corp., N. Y. (1934 and 1937).

* In this reaction a methanol catalyst is employed. Whether or not CO_2 is added, nearly a quantitative amount of carbonate is formed. Part of the water gas introduced reacts according to

$$CO+H_2O=CO_2+H_2,$$

and this CO_2 reacts with the CaO produced.

10) I. G. Farbenind. A. G., G. P. 479829. Since the equation of the reaction is not given, it has been assumed as written.

11) Neuman, Brit. P. 326812 (1928); O. Fuchs and W. Querfurth, G. P. 594672; Deutsche Gold- und Silber-Scheideanstalt vormals Roessler, Brit. P. 478141 (1938), (*C.A.*, 32, 4610 (1938). In the last patent, mainly the normal butyl alcohol has been prepared at 10—100 atmosphere pressure in the pre-

butyl alcohol, according to the reactions as written, at 100, 300, and 500°C are given and they are plotted in Fig. 1. All these reactions, with the exception of 1 (and, perhaps, 3 although some evidence of the formation of higher alcohols have been obtained from our low pressure experiments[3]), are possible not only in theory but also in practice.

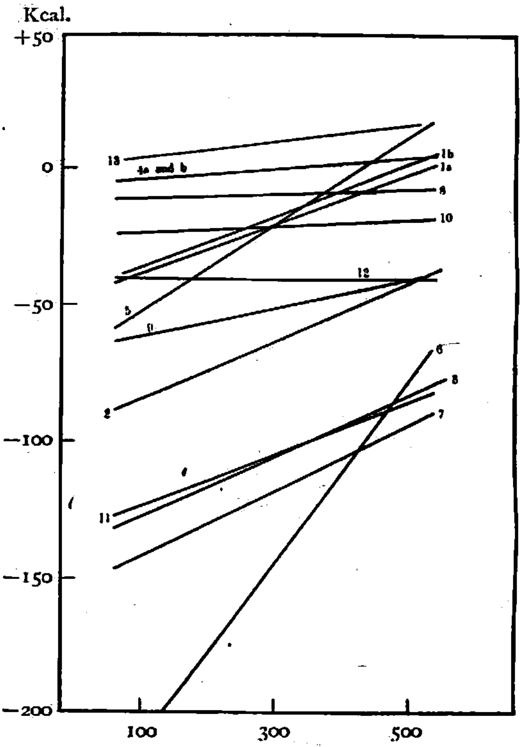

Fig. 1. ΔF vs Temperature.

As can be readily seen from Table III and Fig. 1, in all reactions involving the carbide, the free energies of the reactions are much greater, by 40 to 120 Kcals., than those not containing it. Take, for example, reactions 2 and 3 where the alcohols are prepared from ordinary and nascent acetylene molecules, respectively, in which there is a difference of 40 Kcals.; reactions 5 and 6 in which the alcohols are synthesized from a mixture of carbon monoxide and hydrogen, a difference of 120 Kcals. takes place; reactions 8 and 9 in which the higher alcohols are formed from ethyl alcohol, there is a difference of approximately 40 Kcals.; and, finally, reactions 10 and 11 where a mixture of methyl and ethyl alcohols is

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sence of a catalyst consisting mainly of magnesium, containing a small amount of other metal or oxide, such as Mn, Fe, Cr, W, Sn, Ni, and Co.

† In this case either almost all normal or a mixture of normal and iso-butyl alcohol can be prepared.

12) O. Fuchs and W. Querfurth, U. S. 2050788, (*Chem. Abst.*, 30, 6758 (1936)); Deutsche Gold- und Silber-Scheideanstalt vormals Roessler, G. P. 674751 (1939), (*Chem. Abst.*, 33, 6874 (1939)). In the latter patent, a mixture of methyl and ethyl alcohols is treated with H_2 at 200—350°C in the presence of a catalyst consisting principally of MgO with a small amount of one or more catalytically active metal oxides or metals, such as Al_2O_3 or CuO, to give higher alcohols. The pressure may be ordinary or up to 30 atmospheres.

‡ By this method principally iso-butyl alcohol is prepared whether or not a catalyst is present.

13) P. Frolich and Wiezewich, *Ind. Eng. Chem.*, 24, 13 (1932).

14) D. F. Smith and L. L. Hirst, *ibid.*, 22, 1037 (1930). Under elevated pressures and at about 300°C methanol is produced. This reaction is not a part of the Table proper, but has been included here for a future reference.

used as a starting material for the formation of the butyl alcohols, there is a difference of 80 Kcals. between the reactions involving and not involving the carbide. These differences correspond to, in terms of the logarithm of the equilibrium constant, which is related to the free energy by the relation, $\Delta F = -RT \ln K$, from 15 to 46 fold increase at 300°C; in other words, there will be a tremendous increase in the possibility of synthesizing the alcohols.

It is interesting and instructive to compare again the reactions 5 and 6. In the absence of the carbide the free energy of reaction decreases from -52500 at 100°C to $+13400$ at 500°C. What this means is that, as the temperature is increased, the tendency for the alcohol formation decreases rapidly, and at about 400°C the free energy becomes zero. In practice, however, the reaction is usually carried out above 400°C[15], and in order to off-set the decrease in the free energy by the increase of the temperature (to increase the rate of reaction) higher pressures are employed.

The effect of pressure on the equilibria for the comparative reactions,

$$4CO + 8H_2 = \text{iso-}C_4H_9OH + 3H_2O \qquad (5)$$

and

$$4CO + 8H_2 + 3CaC_2 = \text{iso-}C_4H_9OH + \underset{\lfloor\xrightarrow{\text{Polymerize}}}{3C_2H_2} + 3CaO, \qquad (5')$$

in which the carbide is added, may be roughly seen from the following simple calculation. In both reactions the gases were assumed ideal and the ratio of CO to H_2 remained 1 to 2 throughout, and in the latter reaction, furthermore, the nascent acetylene molecules polymerized into a product with a very low vapor pressure. Under these assumptions, the equilibrium constants of the reactions may be written, respectively,

$$K = \frac{P_{(alc)} P_{(H_2O)}^3}{P_{(CO)}^4 P_{(H_2)}^8} \quad \text{and} \quad K' = \frac{P_{(alc)}}{P_{(CO)}^4 P_{(H_2)}^8}$$

where $P_{(alc)}$, $P_{(H_2O)}$, $P_{(CO)}$, and $P_{(H_2)}$ are, respectively, the partial vapor pressures of alcohol, water, carbon monoxide, and hydrogen. From the data given in Table II, ΔF of the reactions (5) and (5′) may be approximately represented by

$$\Delta F = -112019 + 162\,T \quad \text{and}$$

$$\Delta F = -355670 + 301\,T.$$

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[15] G. T. Morgan, R. Taylor, and T. J. Hedley, *J. Soc. Chem. Ind.*, **47**, 117$_T$ (1928), R. Taylor, *J. Chem. Soc.*, 1429 (1934); G. T. Morgan, Hardy, and Procter, *J. Soc. Chem. Ind.*, **51**, 1$_T$ (1932); G. T. Morgan and R. Taylor, *Proc. Roy. Soc.*, A **131**, 533 (1931); G. Natta, *Osterr. Chem. Zeitg.*, **40**, 162 (1937); E. M. Bocharova, B. N. Dolgov, and Z. M. Prokhorova, *Khim. Tverdogo Topliva*, **6**, 665 (1935), (*Chem. Abst.*, **30**, 2171 (1936); I. G. Farbenbind. A. G., G. P. 625757 (1936); H. Tahara, Y. Tatuki, and J. Simizu, *J. Soc. Chem. Ind., Japan* (*Supp. Binding*), **43**, 82 (1940).

[redacted]

Since $\Delta F = -RT\ 2.3 \log K$, by appropriate transpositions,

$$\mathrm{Log}\ \frac{P_{(alc)}}{P_{(CO)}^{4}} = 6121/T - 10.29 + 8 \log P_{(H_2)} \quad \text{and}$$

$$\mathrm{Log}\ \frac{P_{(alc)}}{P_{(CO)}^{4}} = 77742/T - 65.79 + 8 \log P_{(H_2)}$$

result for the reactions 5 and 5′, respectively. The left hand member of the equations may serve as an index for the degree of conversion into iso-butyl alcohol of the reacting gases.

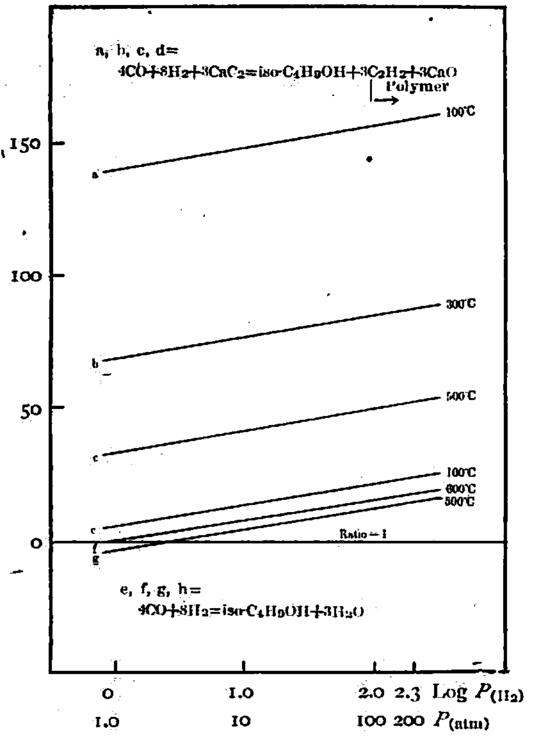

Fig. 2a. Effect of Partial Pressure of Hydrogen.

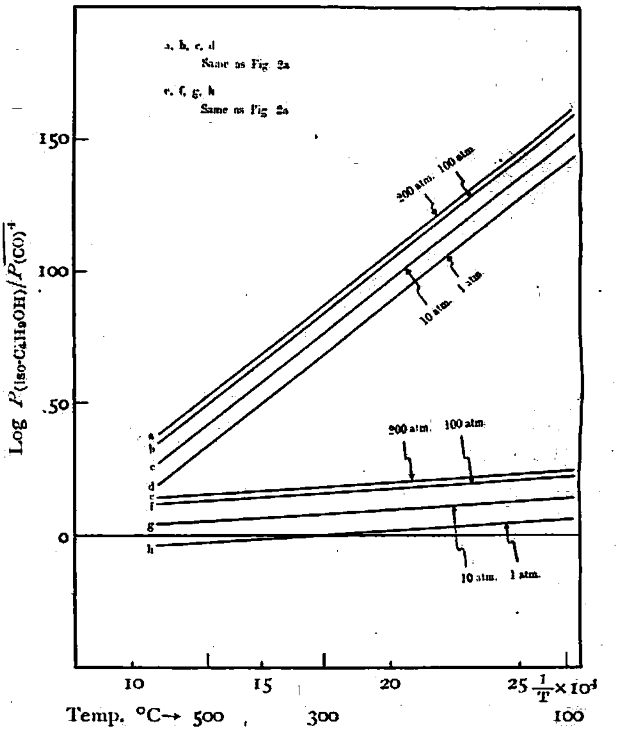

Fig. 2b. Effect of Temperature.

When it is plotted against the partial pressures of hydrogen, Fig. 2 a results; when plotted against the reciprocals of the temperature, Fig. 2 b results. The Figures are self-explanatory, and the effect of pressure on the reactions in the absence and in the presence of the carbide is clear.

Now returning to the comparison which I started to make originally between the reactions 5 and 6, it is seen that, where the carbide is used, $-\Delta F$ is very much larger and even at 500°C it is still about -70 Kcals. This means that not only is the equilibrium further shifted to the right, but also the temperature range in which the alcohols can be synthesized is increased very much, independently of the pressure. Since water is an inhibitor for higher alcohol formation by virtue of its harmful adsorption on the catalyst[16], the presence of the carbide which removes it completely and rapidly is particularly beneficial.

From what has just been considered above, the presence of the carbide may increase the rate* of the alcohol formation, and this would manifest itself even at much lower temperatures than those commonly employed[15]. Evidence for it can be seen from the results of Table IV a where the reaction temperatures have been varied from 300 to 400°C, the rate of the effluent gas from 3 to 25 lit./min., and the carbide content from 300 to 1000 grams per run. There the amount of iso-butyl alcohol** formed per 100 grams of the carbide reacted remains practically the same, as shown in the last column of the Table. In fact, there seems some indication that 400°C may be too high, and the optimum temperature appears to be about 330 to 340°C.

In Table IV b are shown the results of the runs in which the conditions are the same except for the reaction pressures. Unfortunately, during the run of

Table IV a.

Carbide* Paste+Water Gas Reactions at 200 kg/cm².

Exp. No.	Reaction Temp. °C	Wt. (gr.) Carbide	Catalyst No. and Wt. (gr.)	Rate Effluent Gas Lit. per min.	Yield (iso-alc.)§	
					Crude c.c. 100—120° C	c.c. per 100 gr. Carbide
IV$_{\mathrm{A}}$ Ser. 178†	300—305	300	36$_{\mathrm{A}}$, 45	—	9.4	3.1
I$_{\mathrm{CA}}$—5	310	1000	I$_{\mathrm{CA}}$3, 70	10	35.0	3.5
VII$_{\mathrm{A}}$ Ser. 9‡	320	300	6$_{\mathrm{III}}$, 40	—	13.3	4.4
I$_{\mathrm{CA}}$—6	320	1000	I$_{\mathrm{CA}}$3, 70	10	47.5	4.7
I$_{\mathrm{CA}}$—3	330	1000	I$_{\mathrm{CA}}$3, 70	8	51.9	5.2
II$_{\mathrm{CA}}$—10	330	500	II$_{\mathrm{CA}}$, 50	5	23.9	4.8
II$_{\mathrm{CA}}$—16	330	500	II$_{\mathrm{CA}}$, 50	3	28.5	5.7
II Ser. 22	340	500	II$_{\mathrm{CA}}$, 50	3	29.4	5.9
II$_{\mathrm{CA}}$—25	340	750	II$_{\mathrm{CA}}$, 50	3	35.3	4.7
II$_{\mathrm{CA}}$—35	350	500	II$_{\mathrm{CA}}$, 25	5	28.8	5.8
I$_{\mathrm{CA}}$—4	350—360	1000	I$_{\mathrm{CA}}$3, 70	22—25	47.7	4.7
II$_{\mathrm{CA}}$—66	400	500	II$_{\mathrm{CA}}$, 50	10	20.1‖	4.0‖

* Approximately 70% CaC_2 used. Carbide to Oil is 1 : 2 by weight.

† Results in a "static" autoclave.

‡ Also in "static" autoclave; the average pressure was 200 to 160 kg/cm².

§ Mostly iso-butyl alcohol, containing some hydrocarbons of the same temperature range.

‖ Practically pure iso-alcohol. The results of azeotropic distillation (R. Negishi and C. Isobe, *Bull. Chem. Soc. Japan*, 16, 278 (1941).

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[16] P. K. Frolich and D. S. Cryder, *Ind. Eng. Chem.*, 22, 1051 (1930).

* The discussion of the rate here presented is incomplete, since the concept of the activation energy is not explicitly given.

** Practically, only iso-butyl alcohol has been formed.

Table IV b.

Carbide* Paste+Water Gas Reaction at 330°C.

Exp. No.	Reaction Press Kg/cm²	Wt. (gr.) Carbide	Catalyst No. and Wt. (gr.)	Rate Effluent Gas Lit. per min.	Crude iso§-Butanol c.c. per 100 gr. Carbide
II_{CA}—16	200	500	II_{CA}, 50	3	5.7
II_{CA}—56	150	500	II_{CA}, 50	3	3.8(3‖)
II_{CA} Ser. 63	150	500	II_{CA}, 50	3	5.7‖
II_{CA}—49†	50	500	II_{CA}, 50	3	1.5—2

*, §, ‖ have the same significance as in Table IV a.

† Results very rough; about 100—140 grams of carbide reacted.

II_{CA}—49 some mechanical difficulty had developed, and the run was not completed, but the results indicated that iso-butyl alcohol could be produced in the presence of the carbide at fairly low pressures; the rate was slower than that of II_{CA}—16. In the former run, the slowest step in the reaction must have been the formation of methanol from the gas. This point will become more clear when the formation of the alcohols from the lower alcohols is considered.

If the reactions 8 and 9 are compared, some interesting results due to the addition of the carbide come to light. In the absence of it, some catalyst is needed to transform ethyl alcohol into the butyl alcohols (mainly normal), but in the presence of the carbide, there is need of no catalyst to bring about this transformation, and if a methanol catalyst is added, iso-butyl as well as the normal alcohol can be produced, as Table V shows. The role of the catalyst in the above reaction may throw some light on the mechanism of the formation of the higher

Table V.

Ethyl Alcohol+Carbide* Paste at 350°C.

Exp. No.	Press. Kg/cm²	Methanol Catalyst II_{CA} (gr.)	Liquid Below 200°C‖	Products in c.c.		Reacted Carbide (Moles)
				Iso-Butanol† 100 to 110°C	Normal† 110 to 120°C	
II_{CA}—A 43	10	0.0	6.7	2.5	14.5	2
II_{CA}—A 38 (39)	50	0.0	48.4‡	4.0	14.2	2.25
				Total (11.2§)		
II_{CA}—A 40 (41, 42)	50	25.0	74.0	11.0	8.0	3.5
				Total (14.3§)		

* It has the same significance as in Table IV.

† Crude iso- and Normal butyl alcohols (distillates in the temperature ranges given, respectively).

‡ Below 175°C.

§ Practically pure iso- and normal butanols combined (results of solvent analysis).

‖ Excluding unreacted ethyl alcohol.

alcohols. The effect of a methanol catalyst may be that of establishing the equilibrium,

$$(CH_3)_2O = C_2H_5OH,$$

and the ether formed may react with the excess of ethyl alcohol to produce isobutyl alcohol.

There are a number of such mechanisms proposed for the formation of higher alcohols as the reductions of aldehydes and of ketones by Fischer and Tropsch[17]; the aldol condensation proposed by Morgan[18]; the salt formation of Natta[15]; and the progressive condensation proposed by Brown and Galloway[19] and by Frolich[16, 20]. The latter mechanism is, according to Frolich,

$$2CH_3OH = (CH_3)_2O + H_2O$$

$$(CH_3)_2O = CH_3CH_2OH \text{ (by rearrangement)}$$

$$CH_3CH_2OH + CH_3OH = CH_3CH_2CH_2OH$$

$$CH_3CH_2CH_2OH + CH_3OH = C_4H_9OH + H_2O \quad \text{or}$$

$$2CH_3CH_2OH = C_4H_9OH + H_2O.$$

He does not give a definite mechanism for the formation of iso-alcohols, but merely mentions that $(CH_3)_2O$ may be one of the intermediates. He and Cryder could not obtain conclusive evidence that the reaction proceeded through the ether step[16]. Inspite of it, I shall tentatively propose, as an extension of the progressive condensation mechanism for the formation of normal and iso-butyl alcohols in the presence of the carbide, the following:

$$2CH_3OH = (CH_3)_2O + H_2O$$

$$(CH_3)_2O = CH_3CH_2OH$$

$$(CH_3)_2O + CH_3CH_2OH = \text{iso-}C_4H_9OH + H_2O$$

$$2CH_3CH_2OH = \text{n-}C_4H_9OH + H_2O.$$

In the presence of the carbide we have found only a slight amount* of either ethanol or propyl alcohol whether we start out with pure ethanol, with pure methanol, or with their mixtures, in each case with or without a methanol catalyst. From the above fact, it seems more probable that the formation of normal butanol

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17) F. Fischer and H. Tropsch, *Die Umwandlung der Kohle in Oele*, 2, 246 (1924).

18) G. T. Morgan, *Proc. Roy. Soc.*, A 127, 246 (1930).

19) Brown and Galloway, *Ind. Eng. Chem.*, 21, 310 (1929); *ibid.*, 22, 175 (1930).

20) P. K. Frolich, *Ind. Eng. Chem.*, 23, 111 (1931).

* Frolich mentions that intermediate alcohols react more rapidly than methanol, accounting also for the lesser concentration of them in the final product.

is rather from two molecules of C_2H_5OH than from propyl alcohol and methanol, at least in the presence of the carbide.

Finally, I shall discuss briefly the results obtained by starting out with a mixture of ethyl and methyl alcohols in the presence of the carbide, and here, again, there is need of no catalyst. In this case, whether or not a catalyst is used, both normal and iso-butyl alcohols are produced, and though the results are not complete, they seem to indicate that the proportion of the higher alcohols can be varied by varying the ratio of the lower alcohols. This effect is shown in Table VI. The yield of the butyl alcohols by this process is quite satisfactory, as seen in Table VII. In a qualitative way, this process seems to confirm the mechanism of the formation of the alcohols proposed in the preceding section.

Table VI.

Carbide Paste* + Alcohols, Without Catalyst; Reaction Temperature 350°C; Pressure 50 kg/cm².

Exp. No.	Alcohol	Crude Butanol c.c.†		Reacted Carbide (Mole)
		Iso- 100 to 110	Normal 110 to 120	
II$_{\text{CA}}$—A 38 (39)	Ethyl	4.0	14.2	2.25
		Total (11.2‡)		
II$_{\text{CA}}$—A 45 (46)	Ethyl 400 c.c. Methyl 300 c.c.	22.5	6.0	3.0
		Total (13.8‡)		
II$_{\text{CA}}$—A 55	Methyl	16.9	very slight	—

* The same as in Table IV.

† Temperature ranges taken.

‡ Practically pure iso- and normal alcohols (results of solvent analysis).

Table VII.

Effect of a Methanol Catalyst.

Carbide* Paste + Ethyl and Methyl Alcohols at 350°C and 50 kg/cm².

Exp. No.	Methanol Catalyst II$_{\text{CA}}$ (gr.)	Liquid products in c.c.			Reacted Carbide (Mole)
		Below 200°C†	Iso- 100 to 110°C	Normal 110 to 120°C	
II$_{\text{CA}}$—A 45 (46)	None	58.5	22.5	6.0	3
			Total (13.8‡)		
II$_{\text{CA}}$—A 47 (48)	50	59.2	27.2	3.0	3
			Total (19.6‡)		

* The same as in Table IV.

† Exclusive of the unreacted alcohols.

‡ The same as in Table VI.

The satisfactory yield, the lower reaction temperatures, and the less pressure dependence of the new processes here introduced for the first time could have been predicted from the simple thermodynamic considerations, and the recent work on the dehydration of alcohols[21], where mainly ethers are formed, seems to give further assurance that the carbide plays a unique role in the synthesis of normal and iso-butyl alcohols.

Summary.

Iso- and normal butyl alcohols have been synthesized in the presence of calcium carbide. This new synthesis has been proved thermodynamically and practically powerful.

A new mechanism for the formation of the butyl alcohols has been tentatively proposed, and some evidence in support of it has been given.

The strong affinity of the carbide for the water which is always formed along with the higher alcohols in these syntheses plays particularly an important and unique role.

The free energies of reactions for the formations of the butyl alcohols in the presence and in the absence of the carbide have been calculated, and it has been shown that in the former case, the magnitude of $-\Delta F$ is from 40 to 120 Kcals. larger than that of the latter.

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[21] V. N. Ipatieff and R. L. Barwell, Jr., *J. Am. Chem. Soc.* 63, 969 (1941)