(m) CARBON MONOXIDE AND METHANE IN THE CIRCULATION APPARATUS

Experiment 388

Since the decomposition of carbon monoxide into carbon dioxide and carbon is exothermic, carbon monoxide might be thought more likely to react with methane through nascent carbon. In the experiment a mixture of 1 part of carbon monoxide and 2 parts of methane was studied in the circulation apparatus. A freshly prepared catalyst of iron turnings and caustic potash was first tested with water gas. As soon as oil formation had set in, the water gas was blown off and replaced by the carbon monoxide–methane mixture. The temperature was as usual 410°; the pressure 90 atm. The pressure was found unaltered after 3 hours; neither water nor oil was found. The experiment was continued for 5½ hours on the following day, again without yielding any oil or water. It is therefore certain that methane does not react with carbon monoxide. During 5½ hours the pressure dropped by 2 atm. The gas analysis showed that some carbon monoxide was decomposed, which according to the reaction $2CO = CO_2 + C$ would lead to a pressure reduction. Summing up Expts. 343, 347, and 388, we find that methane cannot be converted into liquid compounds by either carbon monoxide or carbon dioxide. As a practical conclusion, in water gas experiments, methane formation should be limited when liquid products are aimed at, since methane, once formed, no longer takes part in the synthol reaction.

(n) EXAMINATION OF PRODUCTS OF REACTION [181]

The object of the researches of this section, dealing with the utilisation of carbon monoxide and water gas, was the production of liquid low-boiling motor fuels regardless of their chemical uniformity.

Contrary to the endeavours of the B.A.S.F. to prepare chemically uniform substances, presumably methyl alcohol, a highly complex mixture was quite welcome to us, as its very complexity would make it more suitable as a motor fuel.

As to the composition of the products, our method yielded an aqueous liquor and an oily layer which contained hardly any hydrocarbons, whilst the B.A.S.F., according to their patents, chiefly find hydrocarbons. These circumstances, as well as the differences in raw materials and in the composition of the catalysts, make it desirable to give further details as regards the reaction products, particularly in view of the complete want of any scientific explanation of the process.

The liquid we obtained consisted broadly of an aqueous and an oily layer, mostly in the ratio of 2 : 1. The aqueous layer generally contained 20 per cent. of a mixture of aliphatic alcohols, aldehydes and ketones, in addition to free fatty acids, the main product being thus of an oily character. By working our apparatus for several weeks, we have prepared larger quantities of these products for closer examination. Their genesis and the theory of the process, which are closely bound up with the knowledge of the many compounds formed, will be discussed at the end of this chapter.

(1) *Acids.*

We have demonstrated the presence of free acids in both the aqueous and oily layers. The aqueous layer was separated from the oil and rendered alkaline with caustic soda. Considerable quantities of iron hydroxide were precipitated. Alcohols, aldehydes and ketones, were distilled off in a Dufton [182] column. The remaining salt solution was acidulated with dilute sulphuric acid and submitted to steam distillation; the steam distillate was exactly neutralised with sodium hydroxide and evaporated to dryness on the water-bath. The salt residue was decomposed with sulphuric acid at 50°, and then exhaustively extracted with ether.

Acids were extracted from the oil by means of 5N-NaOH, and the oil was washed with water which also dissolved considerable quantities of non-acid constituents. The combined alkaline solutions were distilled in a column; the distillate consisted of an aqueous and an oily layer. The residue of sodium salts of the less volatile acids from the oil was decomposed with sulphuric acid, and the acids thus liberated were extracted with ether. This extract was combined with the ether extract of the water-soluble acids and dried with anhydrous sodium sulphate on a shaking machine; the ether was then distilled off with a Vigreux column. We thus obtained the fractions of Table LXXXI; the mean combining weights were determined by titration with sodium hydroxide. The identification of the individual acids, suggested by the titration, has been described elsewhere (*Brennstoff Chemie*, 1923, 4, 277).

TABLE LXXXI

Fraction.	Amount. g.	Mean combining weight.	Fraction.	Amount. g.	Mean combining weight.
100–117°	19·2	—	165–174°	6·3	—
117–119	7·1	62·4	174–176	3·3	100·0
119–140	24·3	65·2	176–185	2·9	—
140–142	11·8	74·0	185–187	6·9	116·0
142–153	5·6	—	187–204	7·1	—
153–155	10·5	82·5	204–206	7·3	146·8
155–162	3·1	—	Residue	7·4	—
162–165	11·6	88·9		134·4	

The presence of formic, acetic, propionic and isobutyric acids was established.

To judge by the higher fractions and their combining weights, higher fatty acids are also present. Their identification was not attempted, but according to their combining weights and boiling points, they go up to $C_8H_{16}O_2$, showing a far-reaching building-up of acids from carbon monoxide.

(2) *Aldehydes.*

For a first orientation of the amounts of aldehydes present in the aqueous and oily liquids, use was made of reduction by means of ammoniacal silver solution. In the water-soluble alcohol-ketone mixture boiling below 87°, 2 per cent. of aldehyde, calculated as propionic aldehyde, was found. The steam-distilled oil was fractionated into 40 per cent. boiling below 99°, containing 7·2 per cent. of aldehyde, and 60 per cent. boiling above 99°, which contained 25·9 per cent. of aldehyde calculated as butyl aldehyde. The presence of propyl aldehyde and of isobutyl aldehyde was definitely proved; normal butyl aldehyde was probably present; formaldehyde was absent.

(3) *Alcohols and Ketones.*

The alcohol–ketone mixture, obtained by distilling the aqueous layer in a Dufton column, was dehydrated with lime and then fractionated. Table LXXXII gives the results after three fractionations.

TABLE LXXXII

Fraction.	Amount c.c.	Amount %.	Spec. grav.
53–58°	37·0	11·3	
58–64	23·3	7·1	
64–68	17·5	5·3	
68–73	29·5	9·0	
73–76	39·1	11·9	0·812
76–79	67·0	20·4	0·820
79–83	45·0	13·7	0·833
83–87	70·0	21·2	0·865

The fractions from 72·5° upwards still contained some water. Fraction 53–58° gave by a further fractionation 25 c.c. of boiling point 55°. The ultimate analysis showed this fraction to consist of about 80 per cent. of acetone and 20 per cent. of methyl alcohol; density $D_4^{20} = 0{\cdot}7977$; both compounds were isolated and identified.

In the higher fraction we suspected the presence of ethyl alcohol, isopropyl alcohol and methyl ethyl ketone. We isolated and analysed ethyl alcohol, normal propyl alcohol (not isopropyl alcohol); further, methyl ethyl ketone, diethyl ketone and methyl *n*-propyl ketone.

Other ketones were identified in the fraction of the steam distilled oil, boiling below 99°; these were diethyl ketone and methyl-*n*-propyl ketone.

(4) *Examination of the Oil.*

The oil, obtained from water gas in the high-pressure apparatus, leaves this apparatus as a clear yellow mobile liquid of a peculiar rather sweet smell. Separated from the aqueous layer and roughly dried through filter paper, it gave the following fractions :—

62–100°	150°	180°	200°
41	73	83	88 per cent.

Almost 90 per cent. of the oil thus boiled below 200°. Its specific gravity was $D^{15} = 0{\cdot}843$. The fraction boiling below 100° contained 4 per cent. of alcoholic water.

To refine the crude oil (1450 grams), the acids were first removed by treatment with caustic soda. The oil was then washed with water, which dissolved about 10 per cent. of non-acid constituents. This aqueous solution gave on distillation with a column a distillate only partly miscible with water. These liquids have, therefore, a restricted solubility in water and go either into the aqueous or into the oil phase, according to proportions and solubility conditions. The crude oil, freed of acids and washed, was steam distilled; 943 grams of steam-distilled oil contained 5 per cent. of water, and 41·6 grams of non-volatile residue were obtained. The aqueous condensate contained a good deal of dissolved oil, which was fractionated from it through a column. The oil volatile in steam gave the following boiling ranges :—

40–100°	125°	150°	175°	200°	225°
40	63	77	87	92	96 per cent.

The oil was a yellow liquid of peculiar smell; the low-boiling fractions were colourless. Concentrated bisulphite solution dissolved 25 per cent. of the oil, and from this solution, on the addition of sodium carbonate, a colourless oil separated, the quantity of which did not agree with the observed diminution of volume. The oil insoluble in bisulphite was washed with sodium hydroxide and water to remove all bisulphite. The oil now had a pleasant smell, but it retained the original yellow colour. To test this oil for hydrocarbons it was diluted with ether and treated with metallic sodium. The sodium was dissolved with copious evolution of hydrogen, and alcoholates insoluble in ether were formed. The oil which had remained unattacked in the ether still contained, according to the ultimate analysis, 15·3 per cent. of oxygen. After four distillations over metallic sodium in a vacuum, the oxygen content was reduced to 0·22 per cent.

$$C_{10}H_{18}.\begin{cases}\text{Calc.: carbon } 86{\cdot}86 \text{ per cent.; hydrogen } 13{\cdot}14 \text{ per cent.}\\ \text{Found: carbon } 86{\cdot}71 \text{ per cent.; hydrogen } 13{\cdot}07 \text{ per cent.}\end{cases}$$

The hydrocarbons thus obtained amounted to 2·5 per cent. of the oil. Expressed in terms of the total steam-distilled oil, the figure would be 2 per cent., and it is not certain whether this small quantity was not the result of the treatment with sodium. There was not enough material for a closer estimation of the hydrocarbons. In any case, the hydrocarbons were quite minor constituents of the oil. As the B.A.S.F. state that their oil consisted chiefly of hydrocarbons, both saturated and unsaturated, their method of procedure must have differed essentially from ours. The preference of the B.A.S.F. for an excess of carbon monoxide over hydrogen, against our large excess of hydrogen, furnishes an explanation for the formation of hydrocarbons. It has been pointed out (p. 240) that carbon monoxide favours the scission of water from alcohols and the formation of olefinic hydrocarbons.

The oil was tested for esters by the determination of the saponification value. After 20 minutes' saponification under reflux with alcoholic potash, 1 gram of the steam distillate from the acid-free crude oil neutralised 4·7 c.c. of *N*10-KOH, corresponding to a saponification number 26·3, or 4 per cent. calculated as acetic ester.

An estimate was finally made of the alcohol content of the oil. The fraction 99–225° of the steam distillate was shaken with bisulphite, which dissolved only 6 per cent. of the oil; in view of the previous findings, the bulk of the fraction soluble in bisulphite was therefore to be looked for in the fractions boiling below 99°. The oil, after washing with a sodium carbonate solution, was boiled under reflux with acetic acid anhydride for 1 hour; the blackish-brown product was treated for half an hour with boiling water in order to decompose the excess of anhydride. The oily layer was then washed with sodium carbonate, passed through a dry filter and distilled. The acetylated oil had the odour of amyl acetate, and gave the following fractions :—

86–99°	125°	150°	175°	190°
3	9	50	78	91 per cent.

Saponification with alcoholic potash yielded 28·9 per cent. of acetic acid.

If the molecular weight of hexyl alcohol is taken as a mean for the alcohols present, as justified by the boiling range of the oil and esters, the (hexyl) alcohol content works out at 50 per cent. of the oil. Renewed boiling of the acetylated oil with water convinced us that our method of preparation yields a product which is free of acetic anhydride. The water used for boiling contained very small quantities of acid, proving that undecomposed anhydride was not present, and that no appreciable saponification had taken place.

Summary of the Reaction Products

The individual compounds obtained in the pressure apparatus from water gas, and their relative quantities, are summarised in Table LXXXIII.

TABLE LXXXIII

Total amount of each group.	Identified so far.	Approx. quantity of identified compounds. % of total products.
10% acids.	Formic acid	0·1
	Acetic acid	2·3
	Propionic acid	2·1
	isoButyric acid	1·0
	Higher fatty acid up to C_8	4·5
29% water soluble alcohols, aldehydes and ketones.	Methyl alcohol	1·5
	Ethyl alcohol	14·5
	Propyl alcohol	—
	Acetone	5·2
	Methyl ethyl ketone	—
11% oil partly miscible with water.		—
48% oil volatile in steam.	Propionic aldehyde	—
	Isobutyric ,,	—
	Di-ethyl ketone	—
	Methyl-*n*-propyl ketone	—
	Higher alcohols up to C_9	15·0
	Ester	2·0
	Hydrocarbons	1·0
2% oil not volatile in steam.	—	—

The summary shows that the products represent an exceedingly complex mixture of diverse aliphatic compounds. The low-boiling constituents, such as acetone, methyl alcohol, and perhaps ethyl alcohol, are easily recoverable by fractional distillation so as to be available for chemical purposes or as solvents. The high-boiling constituents, which cannot be conveniently separated, will be useful as motor fuels.

(*o*) ROAD TESTS OF SYNTHOL [181]

Some road trials were made in order to test the suitability as motor fuels of the oil, called "Synthol" for short, obtained by the reduction of carbon monoxide in the high-pressure apparatus. For this purpose, the crude oil separated from its aqueous liquor was freed of acid and distilled in a fractionating flask up to 200°, when 87 per cent. of distillate was obtained. The bulk of the oil is, therefore, available as a light motor spirit. The constants of the oil thus obtained were :—

$D_4^{20} = 0{\cdot}8289$
Carbon 69·29 per cent.; hydrogen 12·25 per cent.
Gross calorific value 8200 cals. per kg.
Nett calorific value 7540 cals. per kg.

Setting point: separation commences at —30°, the liquid remaining mobile; complete solidification at —90°. A 1 : 1 mixture of synthol and benzene remained clear down to —18°, when separation set in.

Boiling range :—

62–80°	100°	120°	140°	160°	180°	200°
11	37	64	76	84	91	97 per cent.

The flash point of synthol is very low.

The running tests were conducted on a level road; in order to restrict the quantity of fuel required, a 4 h.p. N.S.U. motor cycle, model 1922, was used carrying two persons. The spirit was fed into the carburettor from a small funnel-shaped container. The speed was kept constant at 25 km. per hour. The trial runs were made with neat synthol, and with mixtures of synthol with benzol and benzol-alcohol. The carburettor was adjusted for benzol.

The distances run with 100 c.c. of spirit are tabulated in Table LXXXIV, which also states specific gravity and nett calorific values.

TABLE LXXXIV

Fuel.	Benzol.	Synthol.	Benzol–Synthol 1 : 1.	Benzol–Alcohol–Synthol 1 : 1 : 1.
Spec. grav.	0·879	0·829	0·854	0·840
Nett calorific value per kg.	9570	7540	8580	7740
Nett ,, ,, per l.	8410	6250	7330	6500
Run in km.	2·9	3·0	3·2	2·9

Although synthol has a lower calorific value per unit volume than benzol, it gives more power. It is noteworthy that the mixture of benzol and synthol is still more efficient, showing that the calorific value is not the only determining factor, but that other properties of the fuel mixture must be taken into consideration. It has been suggested [183] that complex mixtures, having a regular boiling curve, are more suitable motor fuels than individual compounds or mixtures with broken boiling curves.

The engine started readily with synthol alone, and with the synthol mixture, and ran very smoothly. It would not run with 1 : 1 synthol–alcohol mixture. In the runs made with synthol alone, the exhaust smelled appreciably of synthol, obviously due to the jet being too large, which had been adjusted for benzol. With proper adjustment of the jet the result with synthol would be still more favourable.

Although the few trials were made merely to give an indication whether synthol is at all suitable as a motor fuel, the mileage obtained shows that synthol is equal to benzol, if not superior to it, by virtue of such properties as its ability to bind water.

(p) Conversion of Synthol into Synthin[181]

Synthol was freed of its constituents boiling below 99°, and the bulk boiling from 99° to 225° was then heated under pressure in an autoclave of 250 c.c. capacity, provided with an internal copper tube. After charging the oil, the air was removed by passing nitrogen in and blowing off. In one experiment 25 grams of oil were heated for 1 hour to 420°. After cooling, 2250 c.c. of gas were blown off, having the following composition :—

CO_2	14·5 per cent.	H_2	9·6 per cent.
C_nH_m	22·7 ,,	CH_4	21·8 ,,
O_2	0·7 ,,	N_2	16·1 ,,
CO	14·6 ,,		

The absorption of the heavy hydrocarbons by sulphuric acid was sluggish and did not reach a constant value in several days; that part of the hydrocarbons which had escaped absorption would be included in the methane. The content of the autoclave (19 grams) consisted of two layers, a dark reddish-brown oily layer (17·5 c.c.) and an aqueous liquid (3·5 c.c.).

In a second experiment * 40 grams of oil were heated for 1 hour to 450°. We obtained 3550 c.c. of gas, and 27·1 grams of liquid products, the oily layer amounting to 27 c.c., the aqueous to 4·5 c.c. A third experiment was made under the same conditions, and the reaction products of the three experiments were united. The water was separated and the oil was fractionated, giving the following boiling range :—

Below 50°	75°	100°	125°	150°	175°	200°	225°	250°	275°	300°
4	10	17	22	35	48	57	65	74	78	84 per cent.

The fractions boiling below 100° had the smell of benzene and coloured sulphuric acid only slightly, except the fraction 75–100°; this fraction was refined with sulphuric acid and distilled.

Of the united fraction boiling above 100°, 50 per cent. was soluble in concentrated sulphuric acid.† The portion insoluble in H_2SO_4 was washed with water and alkali, and then steam-distilled. The distillate had a pronounced petroleum smell. It was submitted to fractionation and yielded :—

120–150°	150–200°	200–270°	Above 270°
24	44	27	5 per cent.

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* It is interesting to compare heating of synthol in the autoclave and at ordinary pressure. If synthol is distilled through an iron tube at rising temperature, slow decompositions set in at 400°. At 450° the decomposition is very brisk, synthol dissociating into hydrogen, carbon, some carbon dioxide and methane. At 480° no more liquid is left, but only carbon and gas.

† Synthol is almost completely soluble in concentrated H_2SO_4.

The fractions insoluble in concentrated sulphuric acid proved to be hydrocarbons of the following composition and density :—

TABLE LXXXV

Fraction.	% C.	% H.	C : H. ratio.	D^{20}_{4}.
Below 50°	84·12	15·44	1 : 2·19	—
75–100	84·48	15·14	1 : 2·13	0·762
120–150	86·89	13·37	1 : 1·83	0·778
150–200	87·74	12·67	1 : 1·72	0·818
200–270	88·43	12·05	1 : 1·62	0·874

A portion of the product of heating under pressure dissolved in sulphuric acid, but separated on dilution with water as oil; this was washed in the customary way and steam-distilled. The steam distillate gave the following fractions :—

100–175°	175–235°	Above 235°
33	54	13 per cent.

The main portion boiling between 175° and 235° contained carbon 79·05 per cent. and hydrogen 11·20 per cent., and, therefore, still contained oxygen.

The bulk of the alcohols, aldehydes and ketones making up synthol can, therefore, be converted into a product in which hydrocarbons predominate. Some of these boil at lower temperatures than the raw material; some have higher boiling points, are not attacked by sulphuric acid, and are saturated. The ultimate analyses show that the C : H ratio increases with rising boiling points. In the lowest-boiling fractions the C : H ratio is about 1 : 2, as in simple naphthenes; the higher-boiling fractions must consist of saturated hydrocarbons built up of several condensed-ring groupings. The process possibly takes place in two stages. In the first, the alcohols split off water to yield the corresponding olefines, fragments of which then reunite, as in the experiment of Ipatiew,[184] under the influence of pressure to naphthenic hydrocarbons. This view was supported by the high olefine content of the gas, and by the fact that lighter and higher boiling hydrocarbons are formed than could be expected from a simple conversion of alcohols into the corresponding naphthenes.

(*g*) Formation of Petroleum from Water Gas

The transition of synthol constituents into hydrocarbons of the petroleum type raises the question of an analogous genesis of mineral oils and, as a special case, the theory of inorganic petroleum formation. The primary conditions for a formation of natural oil from water gas is the occurrence of carbonaceous matter in the lower strata of the earth. Contrary to Moissan's hypothesis, it is immaterial for the synthesis from water gas whether it is in the form of free carbon or carbides. There is ample evidence of the presence of carbon at low depths, and it is manifest that steam penetrating into them would form water gas with the carbonaceous material, or, at somewhat lower temperatures, CO_2 and hydrogen. The escape of such gases from fissures in the earth has actually been observed in volcanic districts. La Croix and Giraud, in 1902, collected the gases issuing from a surface fumarole at Mont Pelé, which Moissan analysed and found to contain: O_2 13·67 per cent., N_2 54·94 per cent., A 0·71 per cent., CO_2 15·38 per cent., CO 1·60 per cent., CH_4 5·46 per cent., and H_2 8·12 per cent. The figures indicate that quite two-thirds of the gas consisted of air. A calculation, eliminating the air constituents O, N, and A, gives, CO_2 50·3 per cent., CO 5·2 per cent., CH_4 17·8 per cent., and H_2 26·7 per cent. We have frequently observed similar mixtures as the residual gas of synthol preparation; for example, in Expts. 93, 139 and others. It is, moreover, possible to produce from a gas of this composition more synthol by contact with iron and bases at about 400°, and under pressure. All the necessary conditions are found in the interior of the earth.

Ramsay[185] has been at pains to establish the presence of traces of nickel in all petroleums as a proof of its formation by catalytic hydrogenation from acetylene, according to Sabatier. This postulate seems hardly called for, since it has been shown in this book that the formation of "synthol," and its conversion into "synthin" takes place most readily in contact with iron. With the knowledge of the occurrence of carbon in the earth's crust, and of water gas emanation in volcanic districts, no further assumptions are needed for admitting the possibility of petroleum formation by a "synthol" process.

Leaving aside Engler's hypothesis of an organic origin of petroleum, the two inorganic theories, *i.e.*, the direct formation of petroleum from carbides (Mendelejeff and Moissan) and the indirect formation *via* acetylene (Sabatier and Senderens), may now be supplemented by the equally feasible "synthol" theory (Fischer and Tropsch). The hypothesis of an inorganic genesis has recently again found advocates.[186] In view of the possible formation suggested, and of the diverse composition of crude oils (paraffinoid, naphthenic and partly aromatic), the need of tracing all occurrences of liquid hydrocarbons in the earth's crust to a single genetic principle does not exist any longer. Every case will have to be considered on its merits. An important point with a petroleum of biochemical origin is the certainty of exhaustion of the deposit. For mineral oil of Plutonic origin, the expectation of life is very different.

(*r*) ATTEMPT AT AN EXPLANATION OF THE SYNTHOL PROCESS

1. *Experimental Conditions which a Theory must Fit*

Any explanation of the result described must pay due regard to two facts. The experiments performed with numerous metals, other than iron, have demonstrated that only those base metals are active which are known as hydrogen carriers, that is, besides iron, nickel, cobalt, and, in a very slight degree, manganese.

The formation of alcohols, oil and the like is successful only when, in addition to these metallic hydrogen carriers, bases and their salts with weak acids are present, and it would appear that the efficiency of oil production depends on their strongly basic character. The base alone, for example, KOH on pumice, is not sufficient; a hydrogen carrying metal must be present.

In contact with iron at a temperature of about 400° under pressure, water gas is converted into a mixture of methane and carbon dioxide (as shown in a previous paper).[187] In the presence of such bases or salts the formation of methane decreases and liquid products appear.

2. *Formation of Formaldehyde*

It may be assumed in all cases of contact with metallic hydrogen carriers that, in the first instance, hydrogen combines with carbon monoxide with formation of formaldehyde. The possibility of this reaction at atmospheric pressure has been demonstrated by Jaeger and Winkelmann.* In experiments made with water gas under pressure, in which liquid products were at once condensed on the hot and cold tube principle, Fischer and Jaeger * obtained considerable quantities of formaldehyde. In the present experiments the formaldehyde has undergone further changes. In the absence of bases or suitable salts, 2 molecules of formaldehyde may be converted into 1 molecule of carbon dioxide and 1 molecule of methane, according to the equation: $2CH_2O = CO_2 + CH_4$;[183] or the reduction to methane may proceed further with formation of 1 molecule of water, which, reacting in its turn with carbon monoxide, yields hydrogen and carbon dioxide. The two possible ways of methane formation lead to the same result, 1 molecule of carbon dioxide being produced for each molecule of methane.

3. *Modification of the Reaction*

In the presence of the bases or salts, the secondary change of formaldehyde may proceed in another way. The investigations of Tropsch and Roelen * have demonstrated that formaldehyde in the presence of sodium carbonate is readily transformed into methyl alcohol at 400° and at ordinary pressure; 2 molecules of formaldehyde yielding 1 molecule of methyl alcohol and 1 molecule of carbon monoxide.

It may be presumed that formaldehyde produced under pressure will also be converted into methyl alcohol by bases and their salts with weak acids, reduction of carbon monoxide under these conditions resulting in the formation of the alcohol, instead of methane and carbon monoxide. An experiment in which para-formaldehyde was vaporised in a current of water gas under a pressure

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* Unpublished.

of 100 atm., and the vapours were passed over pumice impregnated with potassium carbonate at 400°, yielded large quantities of methyl alcohol.

4. *Synthesis by Condensation of Aldehydes*

Whilst there is little doubt as to the primary formation of formaldehyde, and the possibility of directing its transformation or further reduction, the synthesis of butyl alcohol, for example, leaves room for speculation along various lines. In the circumstances, formaldehyde may be directly condensed to larger compounds, analogous to aldol condensation, which is known to be especially favoured by the presence of alkali. Reduction may take place at the same time.

5. *Synthesis by Carbon Monoxide Addition to Alcohols*

Just as carbon monoxide combines with water to formic acid, it might unite with methylated water, *i.e.*, methyl alcohol, to give acetic acid. Suggestions to that effect have been made by Geuther,[189] who, by the action of carbon monoxide upon sodium ethylate at 190°, obtained sodium propionate. There is also a statement by Ljubawin [190] that ethyl acetate heated in a sealed tube in the presence of calcium oxide gave butyric acid as chief product. The statement is interesting, as it is conceivable that carbon monoxide and alcohol do not at once combine to form acids but alkyl formates,[191] which subsequently are transformed into acids by their contact with our alkaline catalyst.

On the assumption that acetic acid is formed from methyl alcohol, either directly or via methyl formate, it is not difficult to explain the appearance of acetaldehyde and ethyl alcohol by progressive reduction of acetic acid under the catalytic influence of the metallic hydrogen carrier. Nor is there any objection to explaining the occurrence of acetone by the catalytic decomposition of acetic acid on the bases or salts of the contact substance,* or the conversion of acetone into isopropyl alcohol by an addition of hydrogen.

Consistently following up the life-history of ethyl alcohol produced by the reduction of acetic acid, the formation of propionic acid by addition of carbon monoxide, and of propyl aldehyde and *n*-propyl alcohol by reduction of the former, must be admitted. That di-ethyl ketone may catalytically result from propionic acid, or that methyl ethyl ketone may be formed from 1 molecule of propionic acid and 1 molecule of acetic acid, is evident, as is also the formation of the corresponding iso-alcohols by addition of hydrogen to these ketones. The appearance of all the products found can be easily explained on the same lines.

The analysis of the oily products indicated that condensation does not proceed very far but is limited to 7 or 8 carbon atoms; at temperatures of 400° and above, the higher members of the aliphatic series are no longer stable, as is known from the cracking of high-boiling into low-boiling hydrocarbons.

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* A portion of the bases of the used catalyst is always found to be combined with acetic, propionic, butyric acids, etc.

The conditions in Geuther's and Ljubawin's experiments are cited in elucidation of the direct and indirect formation from alcohols of acids rich in carbon; these conditions, *i.e.*, entire absence of water, do not obtain in our apparatus. The high pressure under which we work may so much favour the condensation which takes place with diminution of volume, that the presence of steam does not interfere as it would at ordinary pressure. The attempts of von Philippovich * to prepare alcohol and oil at ordinary pressure with the aid of the identical iron–potassium carbonate catalyst failed entirely. High pressure is indispensable for this reaction, as is easily understood on considering that the addition of carbon monoxide to alcohol diminishes the number of molecules to one-half.

6. *Synthesis of Higher Alcohol by Dehydration*

Guerbet,[192] on heating sodium or barium alcoholates for some time with alcohols under pressure to 200° or 250°, observed a scission of water and the formation of higher alcohol, in accordance with the equation :—

$$C_mH_{2m+1}ONa + C_nH_{2n+1}OH = C_{m+n}H_{2(m+n)+1}OH + NaOH.$$

In this way he synthesised quite a number of higher alcohols from the lower, *i.e.*, *n*-butyl alcohol, 2-methyl-pentanol-1, dibutyl alcohol, etc., but did not succeed in condensing methyl alcohol to ethyl alcohol, as, owing to the pressure set up by the decomposition of methyl alcohol, sealed tubes always burst. Repeating Guerbet's experiment with methyl alcohol in a steel autoclave, we obtained, after 24 hours' heating to 240°, dimethyl ether in considerable quantities. At higher temperatures (400° to 430°), in the presence of alkali–iron catalyst, higher-boiling oily products resulted. The decomposition of methyl alcohol into hydrogen and carbon monoxide proceeded, however, too far to be quoted in support of our explanation; for it is conceivable that the higher-boiling products obtained with the aid of the catalyst are formed from the gases liberated by the very mechanism of the reaction which we are trying to explain.

Like Geuther, Guerbet worked with dry alcoholates in the absence of water. The same considerations apply to Guerbet's experiments in explanation of the building-up of higher alcohols from lower ones in our contact apparatus, as to those of Geuther. The assumption would have to be made that the reaction, which at low pressure takes place only in the absence of water, would at high pressure be possible in the presence of water.

7. *Other Possible Explanations*

Without wishing to decide as yet in favour of any one of the suggested interpretations, since several modes of formation may run concurrently,†

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* Unpublished.

† A synthesis by reduction of iron carbonyl with liberation of iron is not likely, although iron, nickel and cobalt form carbonyls.

synthesis by addition of carbon monoxide to alcohols seems to be the most lucid and consistent. It would imply building-up only, and not regeneration of hydrogen, such as would have to be postulated for a formation of acids by the action of alcohols upon the salts in the catalyst, with loss of hydrogen after the manner of Hell's reaction, or for the formation of acetone by the scission of hydrogen from previously formed isopropyl alcohol.

An explanation involving the reduction of carbon monoxide down to a CH_2-group, the union of such groups to olefines, and the hydration of olefines to alcohols seems hardly probable; to account for the aldehydes and acids found, a scission of hydrogen would have to be admitted, which, in view of the tendency to hydrogen addition in operations taking place under high hydrogen pressures, is very unlikely. If olefines were built up of CH_2-groups, one would rather expect any hexylene formed to be hydrogenated to hexane. As a matter of fact, we have found practically no liquid hydrocarbons in these reactions.

It was originally intended to work out a continuous process for the recovery of products which are obtained by preparing formates from carbon monoxide, and by the thermal decomposition of these formates, *e.g.*, lithium formate. In the first experiments, the apparatus had been charged with lithium carbonate on pumice, in the hope that the alternate formation and decomposition of lithium formate might lead to liquid reaction products of carbon monoxide. The experiments were later repeated with potassium hydroxide on pumice. It was found, however, that the desired effect could not be realised in the absence of metallic hydrogen carriers. For these reasons the reactions taking place in our apparatus cannot be explained simply by the intermediate production of formates.

We may conclude this section on the theory of synthol formation by stating that a synthesis by addition of carbon monoxide to alcohols appears, for the present, to be the preferable explanation of the reaction, but we do not claim to have proved this hypothesis definitely.

In presenting this account of our results we have spoken of "synthol" in order to avoid the reiteration of references to "mixtures of reaction products insoluble or not readily soluble in water, and consisting of alcohols, ketones, aldehydes, etc." We recognised that we had not to deal with a uniform chemical compound, nor with a definite class of compounds. The term is employed merely to indicate synthetic substances of an oily character. In justification of our claim to a name for this mixture we may point out that we have been able to elucidate its composition, which differs materially from that of the products obtainable by the process of the B.A.S.F.; the latter consist, according to the statements of the B.A.S.F., predominantly of hydrocarbons, which are obtained only in minute quantities by our method. We have further ascertained that the water-soluble products, methyl alcohol, ethyl alcohol, propyl