84. *Interaction of Carbon Monoxide and Alcohols. Part II. Synthesis of Propionic and* iso*Butyric Acids.*

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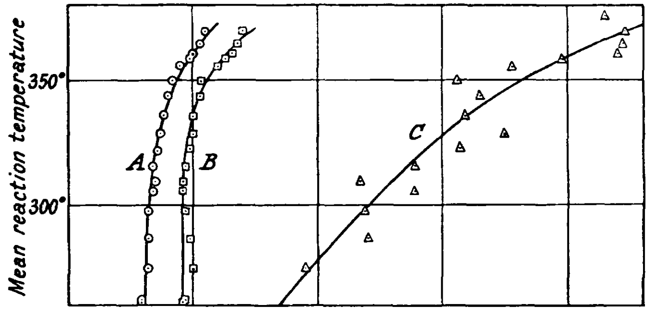
PART I of this series (J., 1934, 1335) was concerned with the synthesis of acetic acid from carbon monoxide and methyl alcohol, a reaction constituting the first stage of Fischer's suggested mechanism (*Ind. Eng. Chem.*, 1925, **17**, 576) for building up carbon chains from carbon monoxide and hydrogen. This communication deals with the second and the third stage of chain elaboration, *viz.*, the conversion of two- and three-carbon alcohols into three- and four-carbon acids respectively :

$$\mathrm{EtOH + CO \longrightarrow Et{\cdot}CO_2H\ ;\ \ CHMe_2{\cdot}OH + CO \longrightarrow CHMe_2{\cdot}CO_2H}$$

Mixtures of alcoholic vapour, steam, and carbon monoxide were passed under a pressure of 200 atm. through phosphoric acid containing a small amount of copper phosphate, a catalyst which had proved efficient for the synthesis of acetic acid (Part I, *loc. cit.*).

FIG. 1.

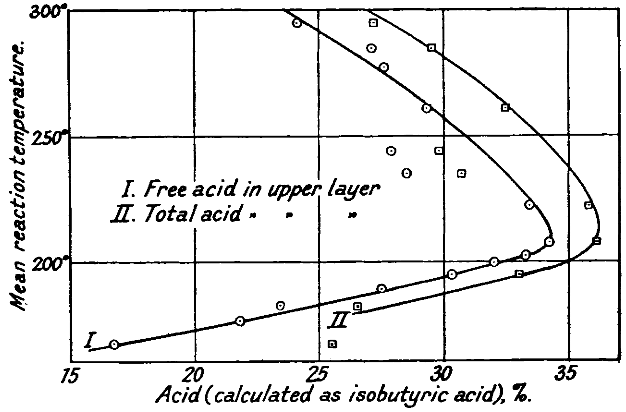


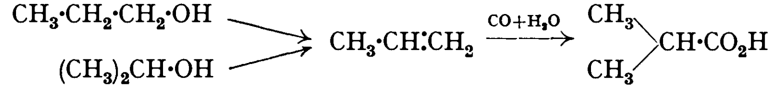
A. Free propionic acid. B. Total propionic acid. C. Ethylenic polymerides.

Between 250° and 370° the product from ethyl alcohol consisted of an upper layer, principally high-boiling polymerides of ethylene, and a lower layer containing water, unchanged alcohol, small amounts of propionic acid and ethyl propionate, and traces of acetaldehyde and volatile hydrocarbons. Fig. 1 illustrates the effect of reaction temperature upon the production of upper layer and propionic acid, both of which are favoured by rise of temperature. It will be seen that ethylenic polymerides were formed at 2—3 times the rate at which propionic acid was produced, and hence, under these conditions, the synthesis of propionic acid from ethyl alcohol is an inefficient process. It seems likely, however, that employment of much higher pressures, *e.g.*, 500—1000 atm., would give favourable results.

Both *n*- and *iso*-propyl alcohol reacted readily with carbon monoxide at comparatively low temperatures, *e.g.*, 150—250°. Two-layer products were obtained which consisted chiefly of acids, unsaturated hydrocarbons, unchanged alcohol, and water. Fig. 2 shows the variation of free and total acid with reaction temperature in the case of *iso*propyl alcohol, and indicates an optimum at 210—215°. On investigating the acidic constituents of the products from these two alcohols, three significant facts were revealed : (a) *iso*butyric acid was the chief constituent, (b) *n*-butyric acid was absent, (c) substantial but variable amounts of higher acids were present. It was concluded that the alcohols as such were not implicated in the reaction with carbon monoxide, but were dehydrated to propylene ; part of the latter then reacted with steam and carbon monoxide, which, in harmony with the modern conception of its structure ($C \leftleftharpoons O$), was added to the β-carbon atom of propylene, giving *iso*butyric acid :

Fig. 2.





$$\left.\begin{array}{l}CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH\\(CH_3)_2CH{\cdot}OH\end{array}\right\rangle CH_3{\cdot}CH{:}CH_2 \xrightarrow{CO+H_2O} \begin{array}{l}CH_3\\CH_3\end{array}\!\!\rangle CH{\cdot}CO_2H$$

Of the residual propylene, part polymerised, and the remainder was found both in the gaseous phase and dissolved in the liquid product, from which it escaped when the pressure was released. A part of the olefinic hydrocarbons formed by polymerisation of proplyene remained unchanged, and the remainder reacted with steam and carbon monoxide to produce higher acids. In agreement with this view, it was found that the higher acids appeared to be members of the series $C_{3n}H_{6n+1}{\cdot}CO_2H$.

Examination of the material consisting chiefly of unsaturated hydrocarbons showed the presence of ketones and probably ethers. These constituents were not completely investigated, but methyl *iso*butyl ketone and di*iso*propyl ketone were identified in the product from *iso*propyl alcohol. The presence of these two constituents suggests two different methods of formation, *viz.*, (a) dehydrogenation of higher alcohols formed either by autocondensation of alcohol or by hydration of a higher olefin :

$$2CHMe_2{\cdot}OH \xrightarrow{-H_2O} CHMe_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3 \xleftarrow{+H_2O} CHMe_2{\cdot}CH{:}CHMe \longleftarrow 2CHMe{:}CH_2$$

$$CHMe_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3 \longrightarrow CHMe_2{\cdot}CH_2{\cdot}COMe + H_2$$

(b) loss of carbon dioxide from two molecules of acid :

$$2CHMe_2{\cdot}CO_2H \longrightarrow (CHMe_2)_2CO + CO_2$$

The following carbon balances were obtained in experiments which, so far as possible, were carried out in a quantitative manner.

		n-Propyl alcohol.		*iso*Propyl alcohol.	
Carbon introduced	As alcohol	1000		1000	
	As CO	74		75	
		1074		1075	
Carbon accounted for	As unchanged alcohol		429		254
	As acids		397		463
	As liquid hydrocarbons, ketones (and ethers ?)		140		173
	As C_3H_6 in gaseous phase		8		60
		974	974	950	950
	Apparent loss	100		125	

In these experiments the greater part of the apparent loss was due to escape of dissolved propylene when liquid was withdrawn from the high-pressure product receiver. The residual gases contained no products other than propylene. Only 57% of *n*- but 75% of *iso*-propyl alcohol reacted, a comparison which suggests the greater ease of dehydration of the latter. Although in the two cases carbon monoxide reacted substantially to the same extent, the acids from *iso*propyl alcohol contained more carbon, owing to the presence of an increased proportion of higher acids.

EXPERIMENTAL.

Apparatus.—The high-pressure circulatory apparatus described in Part I (*loc. cit.*) was used.

Catalyst.—A mixture of copper phosphate (14 g.) and phosphoric acid (700 g. of 87%) was uniformly employed.

Reaction Conditions.—The working pressure was in all cases 200 atm., and the rate of gas circulation was 40 l. of compressed gas per hour. Generation of alcoholic vapour and steam was accomplished by introducing 80% alcohol into the vaporiser.

Ethyl Alcohol and Carbon Monoxide.—Results summarised in Fig. 1 were obtained by examination of samples taken at intervals of 15 minutes while the reaction temperature was gradually raised from 260° to 380°. The rate of vaporisation was constant throughout, and yielded approximately 160 g. of product per hour. The combined upper layers commenced to boil at about 200°, and 34% distilled between 200° and 300° as a light yellow, unsaturated oil. After neutralisation and hydrolysis with a small excess of sodium hydroxide, the lower layers gave an alcoholic distillate which furnished a small amount of volatile hydrocarbons when diluted, and gave acetaldehyde-2:4-dinitrophenylhydrazone (m. p. 155—157°; mixed m. p. 160—161°) when treated with the hydrazine in presence of acid. The solution of sodium salts was evaporated to dryness, and the residue distilled with concentrated sulphuric acid. Water was removed from the distillate with benzene by the azeotropic method. The resulting acid boiled almost entirely between 135° and 142° and consisted of propionic acid (*p*-phenylphenacyl ester, m. p. 92—95°; mixed m. p. 93—96°).

The Propyl Alcohols and Carbon Monoxide.—The data above refer to experiments in which the reaction temperature was 205—210°, and the following quantities of alcohols were passed through the catalyst during 6½ hours : *n*-propyl alcohol, 1118 g. ; *iso*propyl alcohol, 887 g. The products were worked up as follows. After separation of the two layers, the lower was made alkaline and distilled, the alcohol–water azeotrope being obtained. The upper layer was boiled under reflux for 2 hours with a 5% excess of sodium hydroxide solution (50%) and was distilled until all the alcohol and part of the hydrocarbons had passed over. Dilution of the distillate gave an upper layer of hydrocarbons, etc., which was repeatedly washed with water to remove alcohol. Distillation of the aqueous layer and washings gave the alcohol–water azeotrope. Hydrocarbons, etc., were separated from the residual solution of sodium salts and combined with those from the distillate. The combined solutions of sodium salts were evaporated to dryness, and the residue made strongly acid with concentrated hydrochloric acid. After extraction with benzene, the liberated acids were dried azeotropically and distilled.

n-*Propyl alcohol.* The product (above) consisted of 1093 g. of upper layer (C, 56·65; free acid,* 23·9; total acid,* 32·4%) and 282 g. of lower layer (C, 10·4; free acid,* 3·35%). The

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* Calculated on the assumption that the molecular weight of the acid was 88.

upper layer (1003 g.) gave 653 g. of distillate (C, 45·3%) from which 64·3 g. of hydrocarbons, etc., (C, 82·9; H, 13·9%) were obtained; non-volatile hydrocarbons, etc. (C, 80·4; H, 12·9%), weighed 40·9 g. The lower layer (242 g.) furnished 47 g. of *n*-propyl alcohol–water azeotrope (71·7% alcohol). The acids (average molecular weight, 108) distilled as follows: < 150° (7·5 g.); 150—159° (126·5 g.); 159—175° (73 g.); residue (73 g.). The anilide of the acid, b. p. 154·5°, had m. p. 101—102° (mixed m. p. with *iso*butyranilide, 102°). The anilide from the acid of b. p. 163—166° showed no resemblance to *n*-butyranilide (m. p. 94°) and melted at 101—102° (mixed m. p. with *iso*butyranilide, 99—99·5°).

iso*Propyl alcohol.* The product obtained in the quantitative experiment (p. 360) consisted of 726 g. of upper layer (C, 60·15; free acid*, 35·8; total acid,* 38·1%) and 281 g. of lower layer (C, 12·7; free acid,* 5·5%). The upper layer (640 g.) gave an alcoholic distillate (231 g.; C, 54·8%), from which 34·8 g. of hydrocarbons, etc. (C, 84·8; H, 14·5%), were obtained; non-volatile hydrocarbons, etc. (C, 84·5; H, 13·4%), weighed 61 g. The lower layer (242 g.) yielded 43 g. of *iso*propyl alcohol–water azeotrope (87·9% alcohol). Distillation of the acids (average molecular weight = 116) was as follows: 150—159° (131 g.); 159—175° (4 g.); residue (116 g.). The anilide of the acid of b. p. 154·5° melted at 102—102·5° (unchanged on admixture with *iso*butyranilide). The acid of b. p. 163—166° gave an anilide (needles, m. p. 99·5—100·5°) which differed from *n*-butyranilide (rhombs, m. p. 94°) and slightly depressed the m. p. of *iso*butyranilide.

The more complex residual acids were examined as follows. 400 G. of crude acids were boiled under reflux with methyl alcohol (400 g.) and sulphuric acid (24 g.) for 8 hours. The resulting esters were freed from alcohol and acid in the usual manner and fractionally distilled:

B. p.	92—100°	100—130°	130—145°	145—154°	154—170°	Residue
Wt. (g.)	155	14	11	28	10	160

Fraction 1 consisted of methyl *iso*butyrate, and fraction 4 contained a methyl heptoate which, after hydrolysis, yielded a heptoic acid, b. p. 102—106°/14 mm. (*M*, by titration, 130·3. Calc. for $C_7H_{14}O_2$: *M*, 130), whose anilide crystallised from petrol (b. p. 60—80°) in colourless needles, m. p. 68°. The residual esters were distilled further under reduced pressure:

		Found.				Found.	
B. p. /15 mm.	Wt. (g.).	C, %.	H, %.	B. p. /15 mm.	Wt. (g.).	C, %.	H, %.
80—90°	27·2	70·2	11·8	140—150°	13·9	70·9	11·9
90—100	24·5	70·9	11·9	150—170	22·0	71·9	11·8
100—110	8·4	70·4	11·9	170—180	7·9	73·5	12·2
110—120	9·0	70·7	11·8	Residue	8·0	—	—
120—140	20·7	71·1	11·7				

Calc. for $C_9H_{19}\cdot CO_2CH_3$: C, 70·9; H, 11·9%. Calc. for $C_{12}H_{25}\cdot CO_2CH_3$: C, 73·6; H, 12·4%.

Material described above as volatile and non-volatile " hydrocarbons, etc.," was fractionally distilled:

B. p.	100—120°	120—135°	135—150°	150—160°	160—170°	170—180°	180—190°	190—200°	200—210°	Residue
Wt. (g.)	7·7	22·2	16·1	14·0	2·9	6·3	14·1	10·0	12·0	32·0

All the fractions were pleasant smelling, and decolorised bromine water. Analyses gave the following results:

B. p. of fraction	120—135°	180—190°	200—210°
C, %	81·9	83·3	84·1
H, %	14·2	13·7	13·6

Failure to react with metallic sodium showed the absence of higher alcohols. Treatment of an alcoholic solution of fraction, b. p. 100—120°, with 2 : 4-dinitrophenylhydrazine in presence of a few drops of concentrated hydrochloric acid gave orange crystals which, after recrystallisation from light petroleum (b. p. 60—80°), melted at 90—91° alone or mixed with methyl *iso*butyl ketone 2 : 4-dinitrophenylhydrazone. Similarly, the fraction, b. p. 120—135°, gave yellow crystals which, after recrystallisation, had m. p. 88—89°, raised to 92—93° on admixture with di*iso*propyl ketone 2 : 4-dinitrophenylhydrazone (m. p. 94—98°). After complete removal of ketone with 2 : 4-dinitrophenylhydrazine, the fraction of b. p. 120—135° was recovered and distilled. The portion, b. p. 120—135°, still contained oxygen (Found: C, 83·8; H, 14·5%).

Data for Fig. 2 (p. 359) were obtained by examination of samples taken at intervals of 15 minutes while the reaction temperature was slowly increased from 160° to 300°. The rate of collection of product was 180—200 g. per hour. The following table gives further relevant data :

Mean reaction temp.	167°	182°	195°	208°	222°	235°	244°	261°	277°	285°	295°
Acid, %, in lower layer *	4·2	4·1	4·5	5·0	5·5	6·0	6·5	6·9	6·8	6·5	6·2
$\frac{\text{Wt. of upper layer}}{\text{Wt. of lower layer}}$	3·1	2·1	1·9	2·3	1·7	1·3	1·2	0·9	0·6	0·5	0·4

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