292. *Interaction of Carbon Monoxide and Alcohols. Part I. Synthesis of Acetic Acid.*

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In publications from this laboratory relating to catalytic hydrogenation of carbon monoxide (Morgan, Taylor, and Hedley, *J. Soc. Chem. Ind.*, 1928, **47**, 117T; Morgan, *Proc. Roy. Soc.*, 1930, *A*, **127**, 246 ; Morgan, Hardy, and Procter, *J. Soc. Chem. Ind.*, 1932, **51**, 1T) the production of alcohols higher than methyl has been ascribed to an aldol mechanism which postulates formation of higher alcohols from aldehydes by successive processes of aldolisation, dehydration, and hydrogenation. An alternative mechanism (Fischer, *Ind. Eng. Chem.*, 1925, **17**, 576) supposes direct addition of carbon monoxide to alcohols with production of acids which may then undergo reduction to aldehydes and alcohols :

$$\mathrm{MeOH} + \mathrm{CO} \longrightarrow \mathrm{Me{\cdot}CO{\cdot}OH} \xrightarrow{\mathrm{H_2}} \mathrm{Me{\cdot}CHO} \xrightarrow{\mathrm{H_2}} \mathrm{Me{\cdot}CH_2{\cdot}OH}$$

This alternative method of building up carbon chains has received little attention, and since no scientific data concerning it were available, its investigation was undertaken as part of the general scheme of high-pressure research in this laboratory.

The reaction between alcohols and carbon monoxide under pressure and in presence of sodium alkoxides has been shown to yield the corresponding alkyl formate (Stähler, *Ber.*, 1914, **47**, 580; see also Christiansen, J., 1926, 413; B.P. 252,848, 268,890), $\mathrm{R{\cdot}OH} + \mathrm{CO} \longrightarrow \mathrm{R{\cdot}O{\cdot}CO{\cdot}H}$, but the patent literature contains many claims that from methyl alcohol, acetic acid and methyl acetate result when catalysts of the following types are employed : acetates, or materials capable of forming acetates, which yield acetic acid on pyrolysis (B.P. 264,588); non-volatile acids and acidic oxides (notably phosphoric acid; cf. B.P. 283,989; see also B.P. 400,189, 405,282) promoted by compounds of copper and metals of the vanadium–nickel sequence (B.P. 317,867, 343,947); combinations of hydrating and hydrogenating substances (B.P. 254,819, 320,457, 323,475; U.S.P. 1,562,480). These and closely related claims (*e.g.*, B.P. 259,641, 310,438, 340,939, 334,207) specify the use of increased pressure with reaction temperatures up to 450°.

The formation of acetic acid from methyl alcohol and carbon monoxide is an exothermic process, and at room temperature

$$\mathrm{MeOH_{vapour}} + \mathrm{CO} = \mathrm{Me{\cdot}CO{\cdot}OH_{vapour}} + 24{,}840 \text{ cals.}$$

Using Nernst's approximate equation, it may be calculated that under atmospheric pressure equilibrium should be in favour of acetic acid at temperatures up to about 370°, and that at 327° the extent of dissociation of acetic acid into methyl alcohol and carbon monoxide would be decreased from 25% to 4% by an increase of pressure from 1 to 50 atm. Heat considerations would indicate, therefore, that synthesis of acetic acid from methyl alcohol and carbon monoxide should be a simple matter.

The synthesis was achieved in preliminary experiments under a pressure of 150 atm. when carbon monoxide and methyl alcohol were led through phosphoric acid at 320—340°. A typical product consisted of a light-yellow oil (7%) and a colourless upper layer which contained acetic acid (1%), methyl acetate (7%), dimethyl ether (5%), methyl alcohol (34%), and water. With a view to increase the proportion of free acetic acid and maintain approximately constant the state of hydration of the catalyst, subsequent experiments were carried out in presence of steam, added in the form of aqueous methyl alcohol. By using 80% methyl alcohol, a similar product resulted, which contained much less dimethyl ether (1%) and methyl acetate (*ca.* 0·5%), a similar amount of oil (7·5%), 7% of acetic acid, and 27% of methyl alcohol. With an addition of 2% of copper phosphate to the catalyst, the product differed in that oil was no longer present : it contained acetic acid (5·8%), dimethyl ether (1·3%), methyl alcohol (33%), and a considerable amount of methyl acetate (13·5%). The striking fact emerges, therefore, that addition of copper phosphate to the phosphoric acid catalyst not only promotes production of methyl acetate but definitely suppresses oil formation. Further, inasmuch as no enhanced promoting action was observed by a five-fold increase of copper phosphate, suppression of oil formation and promotion of methyl acetate are interdependent, and both oil and acetate have a common precursor.

The oil formed in absence of copper consisted of hydrocarbons (C, 87·8; H, 10·4%) of high b. p. ($< 240°$) and contained hexamethylbenzene. Le Bel and Greene (*Compt. rend.*, 1878, **87**, 260), who obtained a similar oil on passing methyl alcohol over heated zinc chloride, suggested that this alcohol was successively dehydrated to dimethyl ether and then to methylene : $2CH_3\cdot OH \longrightarrow CH_3\cdot O\cdot CH_3 \longrightarrow 2{:}CH_2$, part of which decomposed into its elements while the remainder was converted into complex hydrocarbons by polymerisation with accompanying dehydrogenation. If this hypothesis be adopted, it is only necessary to suppose that copper phosphate is a catalyst for the reaction ${:}CH_2 + CO = CH_2{:}CO$, in order to explain production of oil, its disappearance in presence of copper phosphate, and the formation of acetic acid and methyl acetate : $CH_2{:}CO + H_2O = CH_3\cdot CO_2H$; $CH_2{:}CO + MeOH = CH_3\cdot CO_2Me$.

After use, catalysts always contained considerable amounts of carbon which could have been formed both by decomposition of methylene and by the reaction $2CO \longrightarrow CO_2 + C$, which definitely occurred on the walls of the preceding preheater. Quantitative experiments showed that, on using phosphoric acid containing copper phosphate as catalyst, it was possible by including this free carbon to account substantially for the initial methyl alcohol. The residual carbon monoxide was but little contaminated with gaseous products, which included small amounts of carbon dioxide and methane.

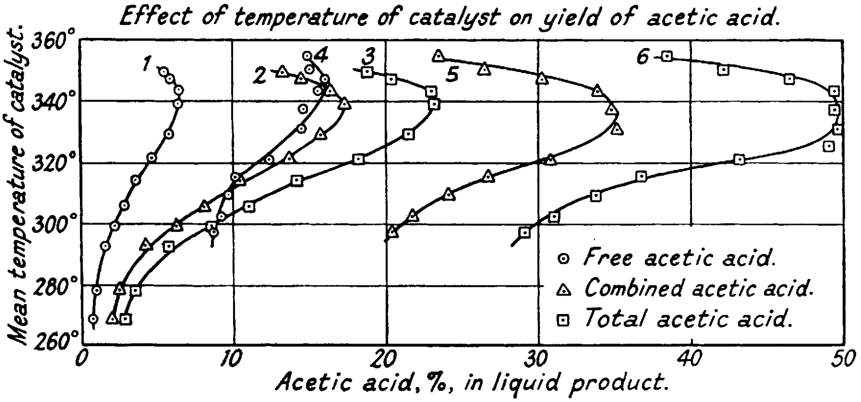
Experiment showed that yields of free and combined acetic acid varied considerably with alteration in operating conditions, and since data were required for conditions approaching the optimum for the apparatus, it was necessary to investigate the effect of each of the various factors. To simplify this problem, 80% methyl alcohol and the same catalyst, *viz.*, 87% phosphoric acid containing 2% of copper phosphate, were used throughout these experiments. In Fig. 1 is shown the influence of catalyst temperature upon yields of free (Curves 1 and 4), combined (2 and 5), and total (3 and 6) acetic acid in two experiments under widely differing conditions. An optimum temperature of 330—340° is indicated. Three series of experiments were then carried out in which pressure, rate of gas circulation, and amount of catalyst were each varied in turn, and yields of free and total acetic acid were determined for various rates of vaporisation of aqueous methyl alcohol. Since it was impossible to measure rate of vaporisation, rate of collection of product was substituted as a first approximation. The results are shown in Figs. 2, 3, and 4, in which percentage of acetic acid is plotted against rate of collection of product. The curves so obtained are fairly characteristic of the operating conditions, and serve excellently for purposes of comparison. It is seen that conversion of methyl alcohol into acetic acid is favoured by increase in (1) pressure, (2) rate of gas circulation, and (3) amount of catalyst. With these three factors increased to the limits set by the apparatus, experiments were then made at a catalyst temperature of 330° in order to test efficiency of catalyst over a considerable period. Results are shown in Table I for a two-

TABLE I.

Time, hours	1	2	2½	3	6	8	12
Free acetic acid, %	18·9	17·5	16·6	21·4	20·7	19·5	22·0
Combined acetic acid, %	9·2	24·1	28·9	29·0	28·1	26·1	27·9
Total acetic acid, %	28·1	41·6	45·5	50·4	48·8	45·6	49·9

day experiment, during which the catalyst was allowed to cool over-night after use for six hours. Efficiency of catalyst steadily increased during the first 3 hours, and then remained fairly constant, excepting at the commencement of the second day when the observed decrease may well be attributable to interruption.

FIG. 1.



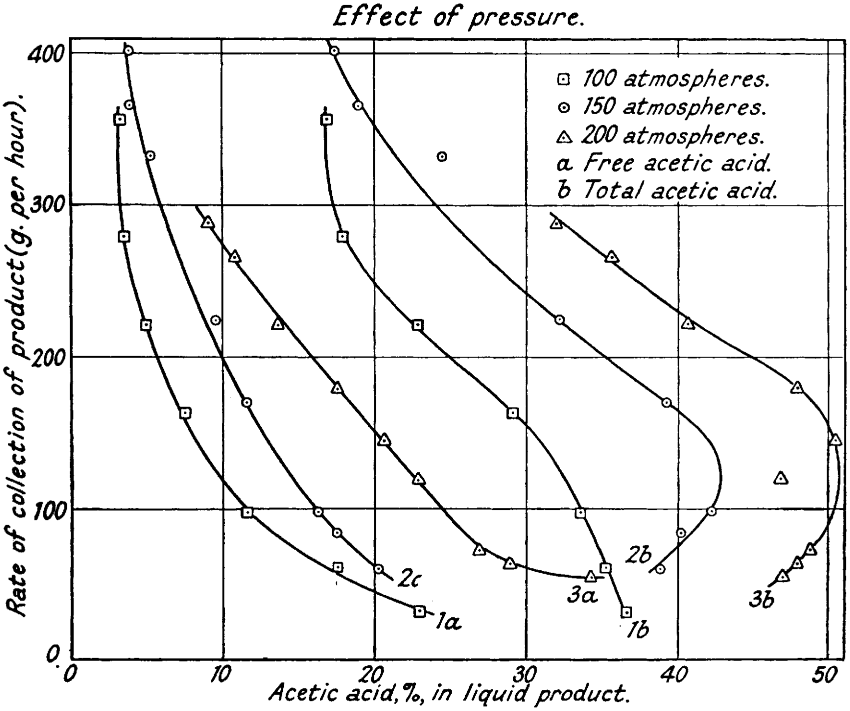
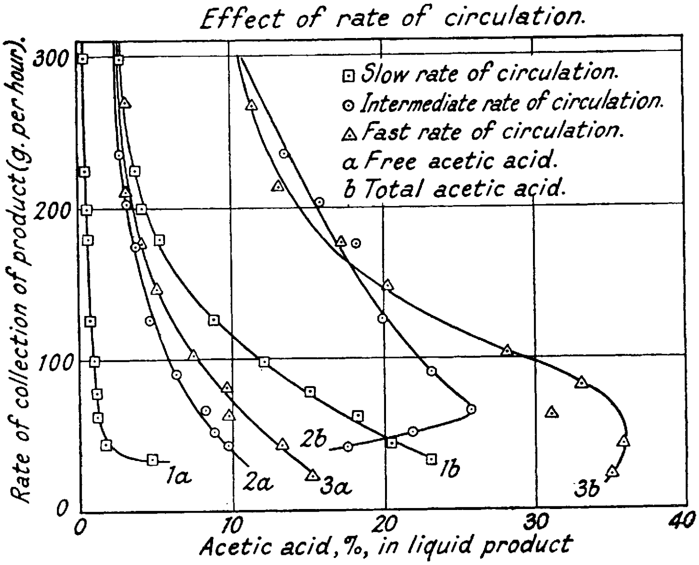


FIG. 2.

Finally, using the optimum conditions for the apparatus, quantitative experiments were carried out, in one of which 1·6 kg. of acetic acid (free and combined) were produced in 14 hours by using as catalyst a mixture of 700 g. of 87% phosphoric acid and 14 g. of copper phosphate. Methyl alcohol passing through the catalyst was accounted for as follows: converted into acetic acid, 44·9; converted into dimethyl ether, 9·5; converted into free carbon, 4·8; unchanged, 35·8; loss, 5·0%. There can be little doubt that dimethyl ether is an intermediate, since its concentration in the circulatory gases was always low (*ca.* 1%) and its total amount decreased if the product were withdrawn from the high-pressure receiver at longer intervals, the percentage of acetic acid being simultaneously increased. Neglecting, therefore, formation of dimethyl ether, the yield of acetic acid calculated on methyl alcohol consumed was 82%, *i.e.*, 44·9 × 100/(44·9 + 4·8 + 5·0). In the above experiment, the rate of circulation was 40 l. of compressed gas per hour. Hence, during 14 hours, 5000 moles of carbon monoxide were passed through the catalyst in producing 26·5 moles of acetic acid, *i.e.*, the conversion of carbon monoxide per passage was 0·5%. This figure is probably governed by efficiency of contact with the catalyst and not by the equilibrium for the reaction.

FIG. 3.



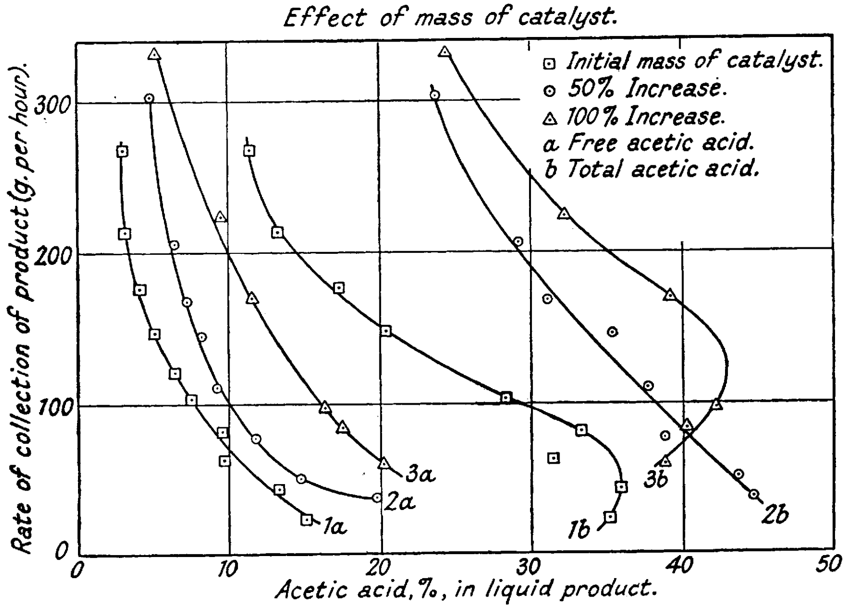


FIG. 4.

EXPERIMENTAL.

Apparatus.—The high-pressure circulatory apparatus, shown diagrammatically in Fig. 5, consisted of the first preheater P_1, vaporiser V, the second preheater P_2, reaction vessel A, condenser C, high-pressure product receiver R_1, and circulating pump O; P_1, P_2, and V were electrically heated, and A gas-heated. Methyl alcohol was introduced into V under working conditions by manipulation of the hand-pump P, together with suitable operation of valves T_1 and T_2. The liquid level in V was adjusted by cautiously opening valve T_3 until liquid ceased to escape through a sight glass on the low-pressure side. Internal arrangements of A are shown to scale in Fig. 6; Q is a loose-fitting silica liner in which the catalyst was placed, I a silver inlet tube, S a silver-sheathed thermocouple pocket, and E the exit. P_2 was of large capacity in order to trap the catalyst should suck-back occur. The product was withdrawn from R_1 into a low-pressure receiver R_2 by opening the valve T_4, whereupon gases liberated from solution escaped through the low-pressure waste pipe W. In quantitative experiments, large glass absorption tubes containing sulphuric acid were connected to W in order to collect dimethyl ether. Speed of circulation was adjusted by means of the circulator by-pass valve, T_5, while pressure was maintained by opening valve T_6, which communicated with high-pressure carbon monoxide storage.

FIG. 5.

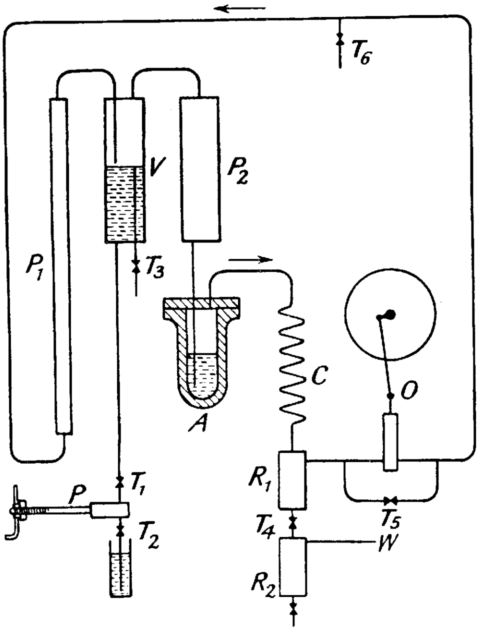
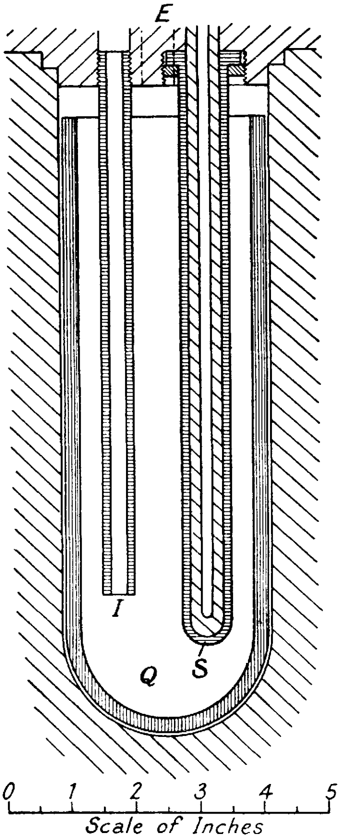


FIG. 6.



Materials.—The carbon monoxide was prepared by the action of concentrated sulphuric acid on 80% formic acid, and was at least 99·5% pure. B.P. Phosphoric acid (*d* 1·75) was used.

Qualitative Examination of Products.—Products were neutralised with sodium carbonate and distilled, dimethyl ether (b. p. −23°), methyl acetate–methyl alcohol azeotrope (b. p. 54°), and methyl alcohol being obtained. Traces of methyl formate were present, since the first runnings reduced ammoniacal silver oxide solution. The azeotropic mixture was shaken with a saturated solution of calcium chloride, dried over calcium chloride, and left in contact with metallic sodium for several days. Distillation gave methyl acetate (b. p. 57·2°), which was further identified by conversion into *p*-phenylphenacyl acetate, m. p. and mixed m. p. 108·5°. The aqueous residue from the distillation was evaporated to dryness, and distilled from concentrated sulphuric acid, whereby acetic acid was isolated. After redistillation from sulphuric acid, glacial acetic acid was obtained. It was converted into *p*-phenylphenacyl acetate, m. p. and mixed m. p. 108·5°.

The upper layer of oil-containing products was similarly treated, whereas the lower was shaken with water and dried over sodium sulphate. On distillation, a colourless oil (b. p. 240—270°) was obtained which partially crystallised in the condenser. The crystals were pressed on porous tile, and after crystallisation from alcohol melted at 159—160° (Found: C, 88·1; H, 11·3; *M*, 160, 166. Calc. for $C_{12}H_{18}$: C, 88·8; H, 11·2%; *M*, 162), mixed m. p. with authentic hexamethylbenzene (kindly supplied by Mrs. K. Lonsdale, of the Royal Institution) 159—162°; picrate, m. p. 170°.

Quantitative Examination of Products.—Acetic acid and methyl acetate were determined by titration, followed by quantitative saponification with *N*/2-methyl-alcoholic potash. Dimethyl ether and methyl alcohol were estimated by carefully hydrolysing the ester with concentrated caustic soda solution, the ether evolved being collected in sulphuric acid. Methyl alcohol was then recovered by distillation, and determined by means of the specific gravity.

Experimental Conditions.—The results shown in Figs. 1—4 and in Table I were obtained in experiments under conditions given in Table II.

TABLE II.

		Catalyst.					
		87% H_3PO_4, g.	$Cu_3(PO_4)_2$, g.	Reaction temp.	Press., atm.	Rate of circulation (l. of compressed gas per hour).	Rate of collection of product (g. per hour).
Fig. 1.	Curves 1, 2, 3	350	7	Varied	150	17	130
,,	,, 4, 5, 6	700	14	,,	200	40	170
Fig. 2.	,, 1*a*, 1*b*	,,	,,	315—318°	100	,,	Varied
,,	,, 2*a*, 2*b*	,,	,,	,,	150	,,	,,
,,	,, 3*a*, 3*b*	,,	,,	,,	200	,,	,,
Fig. 3.	,, 1*a*, 1*b*	350	7	,,	150	,,	,,
,,	,, 2*a*, 2*b*	,,	,,	,,	,,	4	,,
,,	,, 3*a*, 3*b*	,,	,,	,,	,,	17	,,
Fig. 4.	,, 1*a*, 1*b*	,,	,,	,,	,,	40	,,
,,	,, 2*a*, 2*b*	525	10·5	,,	,,	,,	,,
,,	,, 3*a*, 3*b*	700	14	,,	,,	,,	,,
	Table I	,,	,,	328—332	,,	,,	160

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