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HOMOGENEOUS HYDROGENATION OF CARBON MONOXIDE

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A. INTRODUCTION

.This article reviews the progress towards production of alcohols by homogeneous hydrogenation of CO. It is evident from the very large grants made by the U.S. Department of Energy [1] to study the gasification of poor quality coal that the capacity to produce synthesis gas, i.e. $CO + H_2$, will probably increase drastically over the next 10 years. It will therefore become cheaper and be an ideal source for chemicals as well as fuels. Convention-

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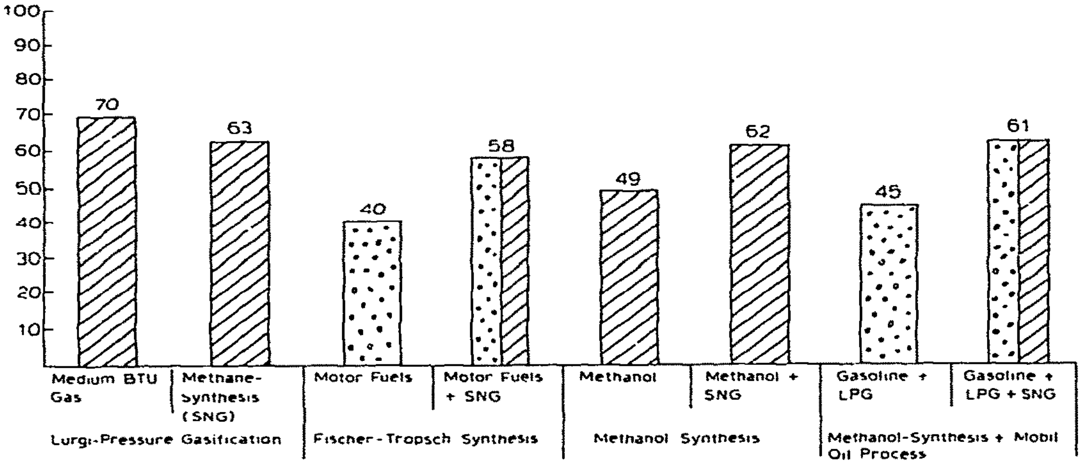


Fig. 1. Thermal efficiencies of proven coal conversion processes. (Adapted from H. Hiller and O.L. Garkisch. Hvdrocarbon Processing, 1980, p. 238.)

ally, syngas, depending on its source, is used to make methanol, methanol and ammonia [2] or methane. Only in South Africa where the Sasol technology is used to convert syngas directly into petroleums, diesel fuels and alcohols by a Fischer–Tropsch [3] heterogeneous route, is a substantial liquid fuel requirement produced from coal (Fig. 1).

The combination of methanol–ammonia plants takes account of the hydrogen-rich nature of natural gas based (methane) syngas (eqn. (1)).

$$CH_4 + H_2O \xrightarrow[\sim 850°C]{Ni} CO + 3\,H_2, \qquad \Delta H_{298} = 206 \text{ kJ mol}^{-1} \tag{1}$$

Syngas derived from coal gasification is not so hydrogen-rich (eqn. (2)).

$$C + H_2O \xrightarrow[\sim 1000°C]{[O_2]} CO + H_2 + [CO_2], \qquad \Delta H_{298} = 130 \text{ kJ mol}^{-1} \tag{2}$$

The gas mixture thus produced has to be freed from sulphur compounds and the gas shifted (eqn. (3)) before it is suitable for methanol or methane production.

$$CO + H_2O \xrightarrow[\sim 450°C]{(Fe_3O_4)} CO_2 + H_2, \qquad \Delta H_{298} = -40 \text{ kJ mol}^{-1} \tag{3}$$

Carbon gasification is very endothermic (eqn. (2)) and up to 40% of the calorific energy of the coal may be used to drive the reaction to the right-hand side [2] (Fig. 1). The process thus consists of burning coal in steam with limited supplies of oxygen and purifying and shifting as described [4], consequently, large quantities of CO_2 are produced.

The loss of fossil carbon as CO_2 is a major problem; as in all combustion the reconversion of CO_2 to more reduced forms of carbon is maintained only by photosynthesis (eqn. (4)).

$$n\,CO_2 + n\,H_2O \xrightarrow{2n\,h\nu} (CH_2O)_n + n/2\,O_2 \tag{4}$$

The alternative sources of retrieving CO_2 are basically gas shift reactions of one sort or another and do not avoid the eventual loss of fossil energy. The methanol gas shift reaction [5] (eqn. (5)) is interesting because it has a positive enthalpy at much lower temperatures than the water gas shift reaction.

$$CH_3OH + CO_2 \xrightarrow[\sim 200°C]{Cu} 2\,CO + H_2 + H_2O, \qquad \Delta G_{500} = -1\ \mathrm{kJ\ mol^{-1}} \tag{5}$$

Alternatively, with copper or nickel based catalysts CO_2 can be hydrogenated to methanol [6] or methane [7]; a more formidable practical task would be the application of the Boudouard [8] reaction (eqn. (6)) in molten metal salts.

$$CO_2 + C \rightarrow 2\,CO, \qquad \Delta H_{298} = 170\ \mathrm{kJ\ mol^{-1}} \tag{6}$$

It is evident that the use of syngas to produce chemicals and fuels must be viewed as a more economically convenient use of fossil carbon than as a solution to the energy problem. The recycling of CO_2 and H_2O still depends on non-fossil energy sources such as sunlight, tides, winds, temperature gradients and nuclear power.

B. HOMOGENEOUS ROUTES TO CHEMICALS AND FUELS FROM SYNGAS

The formation of ethylene glycol, ethanol and methanol directly from syngas has been achieved by homogeneous catalytic reactions (eqns. (7)–(10)). None of the processes is near to a commercial application because the pressures used (normally > 200 bar) and/or the poor selectivities are too far from economic reality.

$$2\,CO + 3\,H_2 \rightarrow (CH_2OH)_2 \tag{7}$$

$$2\,CO + 3\,H_2 \rightarrow CH_3CHO + H_2O \tag{8}$$

$$2\,CO + 4\,H_2 \rightarrow CH_3CH_2OH + H_2O \tag{9}$$

$$CO + 2\,H_2 \rightarrow CH_3OH \tag{10}$$

The formation of ethanol [9] even at 250 bar is far too slow to be of commercial interest; for ethanol and acetaldehyde the homologation of methanol with syngas represents a more attractive alternative process (eqns. (11) and (12)). It must be emphasized that the *heterogeneous* production of methanol has already an established technology [10]; being a C-1 hydrocarbon its production is not subject to selectivity problems associated with the formation of C_2 and higher molecules [11]. Methanol is therefore cheap.

Methanol can be oxidized to formaldehyde which can be hydrocarbonylated to glycol aldehyde [12,13] (eqn. (13)).

$$CH_3OH + CO + H_2 \xrightarrow[\sim 200\ \text{bar}]{\text{Co}} CH_3CHO + H_2O \tag{11}$$

$$CH_3OH + CO + 2\,H_2 \xrightarrow[\sim 200\ \text{bar}]{\text{Co}} CH_3CH_2OH + H_2O \tag{12}$$

$$CH_2O + CO + H_2 \xrightarrow[120\text{-}200\ \text{bar}]{\text{Co or Rh}} OCHCH_2OH \tag{13}$$

Hydrocarbonylation processes are fast but selectivities are inadequate in most cases; also notable is that the normal byproduct is water not carbon dioxide.

C. MECHANISTIC ASPECTS OF DIRECT HYDROGENATION OF CARBON MONOXIDE

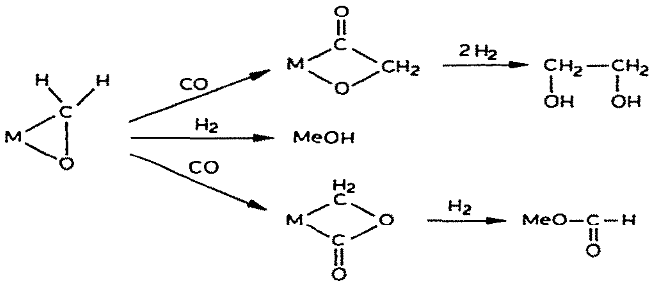
(i) Carbon monoxide activation

The direct conversion of syngas to ethylene glycol and methanol has been much publicized [14] and discussed. There are a series of patents and papers which cover the formation of these molecules in the presence of rhodium carbonyl cluster anions and using polyglymes as solvents [15]. A basic problem is the enormous pressures needed to facilitate reaction (>400 bar). A ruthenium based catalyst was found to catalyse the formation of methanol and methyl formate [16] from syngas, again extremely high pressures are involved (1300 bar). Ruthenium catalysts in acetic acid also catalyse the formation of ethylene glycol ester [17] at pressures of 340 bar.

One commonly invoked initial step for all these processes involves the formation of bound formaldehyde as an intermediate (eqn. (14)) formed by hydrogen attack on a metal carbonyl [17,17a] to generate a formyl.

(14)

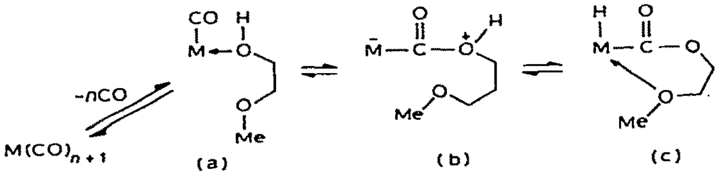
Ethylene glycol could be produced by further carbonylation and hydrogenation; methanol by hydrogenation. Methylformate can be formed by carbonyl insertion into a metal oxygen bond rather than a metal carbon bond (Scheme 1). Formaldehyde intermediates are discussed in the next section.



SCHEME 1

High pressure infrared spectroscopy has been used to identify, under reaction conditions, the cluster $[Rh_6(CO)_{15}]^{2-}$ [15] in the rhodium catalysed glycol formation, and $Ru(CO)_5$ in the ruthenium catalysed glycol acetate formation in acetic acid [17a]. $Ru(CO)_5$ was also detected after depressurizing autoclaves in which methanol and methylformate had formed [16].

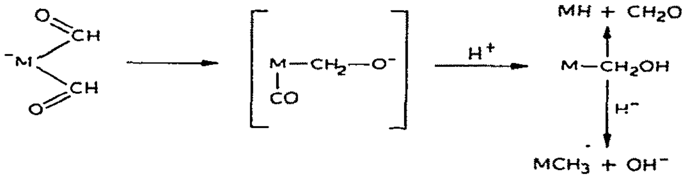
Recent work at lower syngas pressures (< 200 bar) using $Ru_3(CO)_{12}$ in methoxyethanol [18] showed the formation of methanol, acetone and bis(2-methoxyethoxy)methane. Immediately after the reaction, solutions (at 1 atm) showed no terminal or bridging metal carbonyl bands in the infrared spectrum, but these returned slowly over a period of hours leading to $Ru(CO)_5$, $Ru_3(CO)_{12}$ and ruthenium alkoxo gels; similar behaviour was noted for the carbonyls of chromium, iron and cobalt. The inference drawn from these observations was that either ether or alcohol oxygen bound metal complexes may form under reaction conditions which may be more active hydrogenation catalysts than carbonyls themselves. The complexes revert to the more stable metal carbonyls at ambient temperature and pressure (eqn. (15)).



(15)

Infrared data from fresh catalyst solutions after depressurization were indicative of the presence of species like (b) and (c) of eqn. (15). Such a mechanism for initial CO activation forms a viable alternative to formyl group synthesis (eqn. (14)) and is basically an extension of the mechanism proposed for the water gas shift reaction. Attack of alcohols or alkoxide ions on coordinated CO has been long known to generate alkoxo carbonyl species.

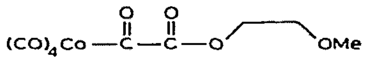
The proposal of formyl intermediates from $CO + H_2$ has its origins in non-catalytic work of Treichel and Shubkin [19], Nesmeyanov et al. [20] and have been exploited elegantly by Casey et al. [21] and Gladysz et al. [22]. The predominant role of metal formyls (which are usually fairly unstable species) appears to be that of hydrogen transfer either to make metal hydrides or hydrogenate organic materials. A rearrangement of *two* formyls on the same metal atom does convert MCHO to MCH_2O^- (Scheme 2) and the reaction may be viewed, in essence, as an inorganic Cannizaro reaction [21].



SCHEME 2

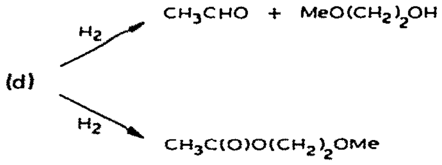
There is kinetic evidence to suggest that the formation of glycol and methanol proceeds by the formyl route, but no formyls have been detected spectroscopically in reacting systems.

By contrast, CO insertion into metal oxygen bonds in homogeneous reactions is a relatively new idea for CO hydrogenation. The compound (d)



(d)

will hydrogenate at 5 bar [9] to produce acetaldehyde and methoxyethanol in 1 : 1 ratio plus unidentified carboxylates; in the absence of hydrogen (d) will rearrange (in an uninvestigated reaction) to again yield carboxylates. The recently reported formation of ethanol from syngas in glyme solvents using $Co_2(CO)_8$ as a catalyst precursor has led to speculation about the source of the ethanol [9]; certainly, most would appear to come from solvent breakdown, but in so doing the solvent fragments by acid catalysed ether cleavage to give alkoxides. These reactions run in CO-rich syngas ($CO:H_2 > 1$) at elevated pressures (230 bar) lead to ethanol and acetates. It is reasonable therefore that compounds of type (d) could be intermediates in this process (Scheme 3).



SCHEME 3

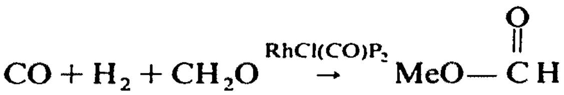
(ii) Bound formaldehyde as an intermediate in direct carbon monoxide hydrogenation

The formation of *free* formaldehyde from syngas is thermodynamically unfavourable

$CO + H_2 \rightarrow CH_2O, \qquad \Delta G_{270} + 27 \text{ kJ mol}^{-1}$

and its decomposition to syngas is catalysed by transition metals. The hydrocarbonylation of formaldehyde yields glycol aldehyde or methyl formate; hydrogenation yields methanol. Methanol and methyl formate can be formed in low yield by reacting paraformaldehyde in *n*-dibutylether with a rhodium complex $RhCl(Co)(PPh_3)_2$; a co-product is syngas [22a].

$$CH_2O \xrightarrow{RhCl(CO)P_2} CO + H_2 \qquad (16)$$



$$CO + H_2 + CH_2O \xrightarrow{RhCl(CO)P_2} MeO{-}\overset{\overset{\displaystyle O}{\|}}{C}H \qquad (17)$$

$$H_2 + CH_2O \xrightarrow{RhCl(CO)P_2} MeOH \qquad (18)$$

If formaldehyde were formed by direct syngas reaction and remained bound to a metal centre it may be thermodynamically stable enough to react further under high syngas pressure (> 200 bar) to yield methanol, methyl formate, glycol aldehyde or ethylene glycol. Formaldehyde is a strong reducing agent and besides hydrocarbonylation reactions it undergoes condensations to sugars of which glycol aldehyde is a precursor. Indeed, base or acid catalysed condensations of formaldehyde have been proposed as a route to ethylene glycol [23,24].

$$2\,CH_2O \rightarrow OHC{-}CH_2OH \qquad (19)$$

These reactions, however, are not highly selective and for the base catalysed reaction crossed Canizzaro reactions occur

$$2\,HCHO + NaOH \rightarrow CH_3OH + HCO_2Na \qquad (20)$$

$$HOCH_2CHO + HCHO + NaOH \rightarrow HOCH_2CH_2OH + HCO_2Na \qquad (21)$$

Acid catalysed condensation reactions yield, besides glycol aldehyde, C-3 and C-4 compounds.

At high syngas pressures (> 200 bar) evidence exists to suggest that rhodium, ruthenium and cobalt catalysed carbon monoxide hydrogenation reactions proceed via bound formaldehyde intermediates. Four observations are relevant.

(a) The association of methanol and ethylene glycol always together in the

Ru, Rh catalysed routes to ethylene glycol imply a formaldehyde precursor, Scheme 1.

(b) The formation of glycerol derivatives at high pressures in the Ru, Rh and Co catalysed reactions. These derivatives could come from condensation of free or bound formaldehyde.

(c) Kinetic evidence above 200 bar indicates a zero order dependence on CO (Ru, Co) and first order in H_2 for the cobalt catalyst reaction and $1\frac{1}{3}$ order in H_2 for the Ru catalysed reaction in carboxylic acid solution. These kinetic data have been taken to support the idea of a mononuclear metal carbonyl precursor and formation of a hydrido formyl complex as a key intermediate [17,25].

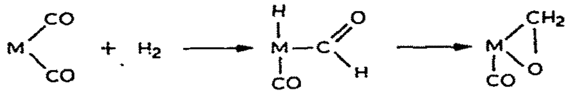
(d) At pressures <200 bar the cobalt catalyst reaction in glyme solvents produces ethanol predominantly for $CO:H_2$ ratios of 1 : 1 (supposedly from hydrocarbonylation of formaldehyde) [25] but increasing the hydrogen to carbon monoxide ratio increases the methanol formed (from zero at $CO:H_2$ 1 : 1) until alkanes start to form ($H_2:CO$ 3 : 1) [9].

Clearly, the formaldehyde route seems quite plausible and certain inferences may be justified:

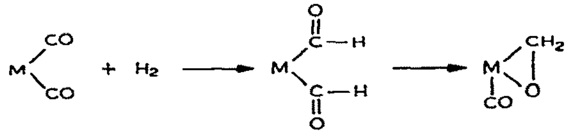
(a) The selectivity in ethylene glycol formed using present catalysts may never become high because of the competing methanol formation, although by judicious addition of a hydrocarbonylation catalyst the selectivity in ethanol + ethylene glycol may eventually be acceptable.

(b) If bound formaldehyde formed is liberated, under certain conditions (e.g., non-coordinating solvents [27]), it may decompose to syngas and hence the rate of formation of glycol and methanol may be below that actually possible. We can judge (superficially at least) the amount of free formaldehyde formed by the amount of glycerol derivatives formed: at high pressures (>1000 bar) this may reach as high as 5% [25].

(c) Since formaldehyde hydrogenates and hydrocarbonylates rapidly under syngas, the rate determining step must precede its formation and may involve the formation of a hydroformyl or a diformyl metal complex [26] (eqns. (22) and (23)).



(22)

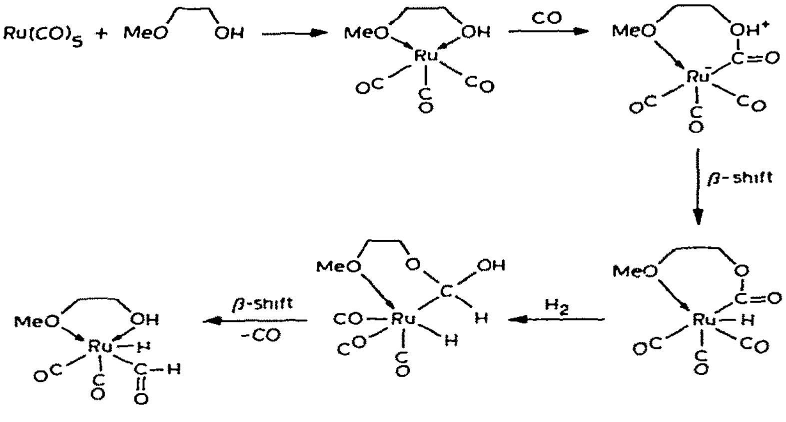


(23)

Reactions 22 and 23 have rate steps which probably depend on hydrogen pressure only.

It is interesting to note that chelating alcohols such as methoxyethanol enhance the rate of methanol formation on ruthenium below 200 bar. A mechanism for CO activation has been proposed (eqn. (15)) and subsequent steps could lead to formaldehyde or methoxy groups by simple β-hydrogen transfer (Scheme 4). A binuclear metal species could produce a biformyl intermediate.

A generalized scheme for carbon monoxide activation in promoting solvents is given in Scheme 13.



SCHEME 4

It is probably true that many group 8 metal complexes will produce glycol and methanol and methylformate if subject to high enough pressures (~ 2000 bar) no matter what solvents are used. This has been illustrated by Keim [27]. These pressures, however, are unrealistic in commercial terms where a maximum working pressure of 100 bar is preferred.

The future of direct homogeneous carbon monoxide hydrogenation on a large scale is thus very speculative, but happily the hydrocarbonylation of methanol and its derivatives already forms the basis of many syngas conversion processes.

D. INDIRECT HYDROGENATION OF CARBON MONOXIDE

(i) Insertion reactions involving methyl iodide

A series of reactions start with methanol and produce C-2 compounds with gas pressures of well below 100 bar. Methanol is cheap and can be used effectively provided the hydrocarbonylations are selective.

Monsanto's [28] now classic carbonylation of methanol to yield acetic acid was the first of such processes (eqn. (24)). Selectivity is essentially 100%.

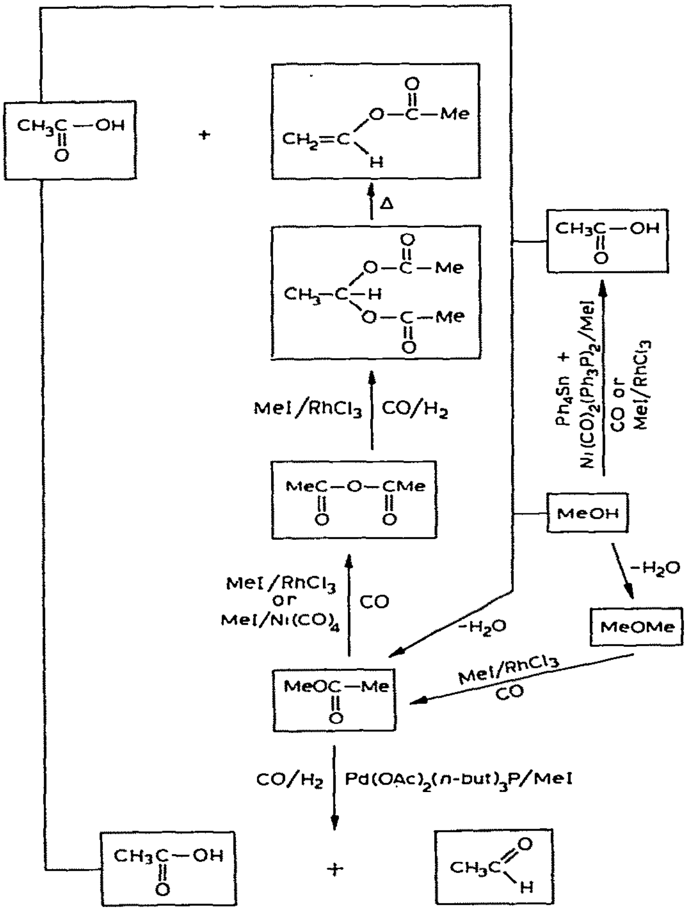
$$CH_3OH + CO \xrightarrow{RhCl_3/MeI} CH_3CO_2H \qquad (24)$$

Dimethylether can be carbonylated to methylacetate [29] which in turn can be carbonylated to acetic anhydride [30]. Methyl acetate can be hydrocarbonylated to ethylidene diacetate [31] which can be converted to vinyl acetate and acetic acid. Methyl acetate can also be hydrocarbonylated to acetaldehyde and acetic acid [32]. Methanol can be carbonylated to acetic acid also using nickel catalyst [33]. These processes were discovered by the Halcon Research and Development Company and are illustrated in Scheme 5.

Thus, two catalytic cycles are set up which convert (a) methanol to acetaldehyde and water and (b) methanol to vinyl acetate and water (eqns. (25) and (26)).

$$\mathrm{MeOH + CO + H_2 \rightarrow CH_3CHO + H_2O} \qquad (25)$$

$$\mathrm{2\ MeOH + 2\ CO + H_2 \rightarrow CH_2{=}CH(OAc) + 2\ H_2O} \qquad (26)$$



SCHEME 5

The normal one-stage cobalt catalysed iodine promoted homologation of methanol works around 200 bar with selectivities around 60–70%. The Halcon hydroformylation of methylacetate works at 40 bar and with the same selectivity.

The formation of acetic anhydride from methanol via methylacetate under anhydrous conditions is the basis of a Tennessee–Eastman–Halcon process in current development.

(ii) Homologation reactions

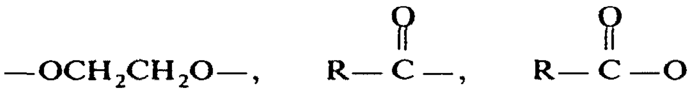
Wender's [34] original experiments to produce ethanol from MeOH with low selectivity using $Co_2(CO)_8$ catalysts were considered interesting but unimportant until the discovery of iodine promotion by Berty et al. [35]; from then on many papers were written and many patents filed on ethanol and acetaldehyde production from methanol [36,37] but the mechanism remains, even today, obscure. It is generally assumed that methyl iodide is formed which subsequently hydrocarbonylates to acetaldehyde and hydrogen iodide, Scheme 9.

The increasing amounts of water formed as the reaction proceeds cause side reactions resulting in acetic acid; acetates and acetals are also formed.

Homologation of acids is achieved via a MeI promoted ruthenium catalyst [38] (Scheme 10). Ruthenium has been used to hydrocarbonylate a variety of oxygen containing compounds including ethers, esters and formates [38a].

Ruthenium is evidently a most versatile catalyst giving rise to

$Me—*$, $—CH_2—*$, $R—O$, $—O—CH_2O—$.



$$—OCH_2CH_2O—,\quad R—\overset{\overset{\displaystyle O}{\|}}{C}—,\quad R—\overset{\overset{\displaystyle O}{\|}}{C}—O$$

species [39] which lead to methane, polymethylene, alcohols, bisalkoxy methane, glycol esters, alkyl formates, esters and acids, by indirect hydrocarbonylation. A negative aspect is the ease of methane formation with ruthenium.

'Homologation' or hydrocarbonylation of paraformaldehyde is a fast reaction on cobalt or rhodium [12,13] based catalysts; glycol aldehyde and methanol are produced. Selectivity is high in glycol aldehyde (eqn. (27)).

---

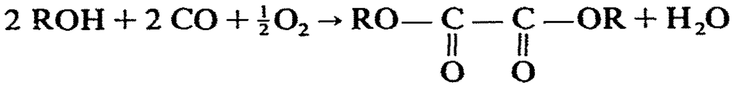
* Ruthenium is an excellent methanation catalyst and also catalyses polymethylene formation, in the heterogeneous phase.

$$\left.\begin{array}{l} \mathrm{CH_2O + H_2 + CO \xrightarrow[DMF]{Rh}} \\ \mathrm{CH_2O + H_2 + CO \xrightarrow[dioxane]{Co_2(CO)_8}} \end{array}\right\} \rightarrow \mathrm{OCH{-}CH_2OH} \qquad (27)$$

The heat of formation of formaldehyde from syngas is negative and so formaldehyde is formed from partial oxidation of methanol, nevertheless, it is a cheap feedstock.

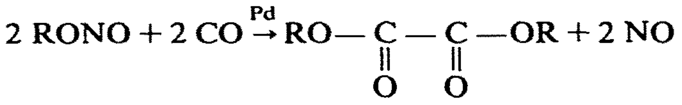
(iii) Oxidative coupling of carbon monoxide and alcohols

A fascinating reaction involving the coupling of two carbon monoxide molecules to give oxalates has been developed using palladium catalysts by the Ube, Montedison and Atlantic Richfield chemical companies [40–42]. The Ube process employs *t*-butylnitrite (formed from *t*-butylalcohol and nitrogen oxides), carbon monoxide and a palladium acetate catalyst. The overall reaction is given by eqn. (28).



$$\mathrm{2\,ROH + 2\,CO + \tfrac{1}{2}O_2 \rightarrow RO{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}OR + H_2O} \qquad (28)$$

The intriguing aspect of this reaction is the use of a reversible gaseous oxidizing agent, N_2O_3. Reactions can be run heterogeneously or homogeneously and the sequence envisaged in the reaction is



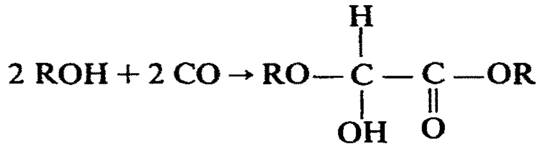
$$\mathrm{2\,RONO + 2\,CO \xrightarrow{Pd} RO{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}OR + 2\,NO} \qquad (29)$$

$$\mathrm{4\,NO + O_2 \rightarrow 2\,N_2O_3} \qquad (30)$$

$$\mathrm{2\,ROH + N_2O_3 \rightarrow 2\,RONO + H_2O} \qquad (31)$$

In the heterogeneous process the NO can be separated from the oxalate and safely oxidized separately and recycled. Methanol can be oxidatively carbonylated to dimethyl oxalate in a Montedison heterogeneous process (eqn. (28)). Yields of 90% are claimed at 60°C and 100 bar [41].

A subsequent hydrogenation of the dialkyl oxalate produces glycol derivatives which can be hydrolysed to glycol and alkyl alcohol for recycling. The use of oxygen in the Ube process becomes unnecessary if modified ruthenium catalysts are used (eqn. (32)).



$$\mathrm{2\,ROH + 2\,CO \rightarrow RO{-}\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}{-}\underset{\underset{O}{\|}}{C}{-}OR} \qquad (32)$$

The copper catalysed oxidative coupling of alcohols and carbon monoxide to yield carbonates has recently been developed [43]. A binuclear copper halogeno-alcoxide species is proposed as the catalyst (eqn. (33)).

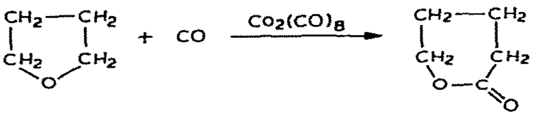
$$2\,\mathrm{MeOH} + \mathrm{O} + \mathrm{CO} \xrightarrow{\mathrm{Cu}} (\mathrm{MeO})_2\mathrm{C{=}O} + \mathrm{H_2O} \qquad (33)$$

Carbonates are invariably byproducts in oxalate synthesis.

E. MECHANISTIC ASPECTS OF INDIRECT CARBON MONOXIDE HYDROGENATION

(i) Cleavage reactions

It has been known for many years that the hydrocarbonylation of tetrahydrofuran with dicobalt octacarbonyl yields butanol; similarly, carbonylation yields delta valerolactone (eqn. (34)) [44].

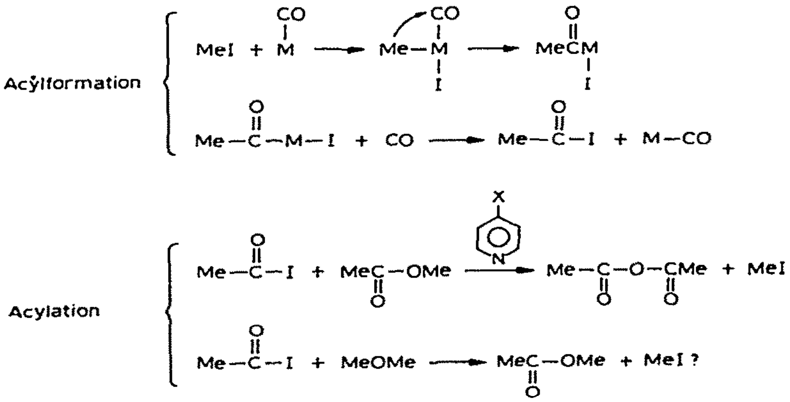


(34)

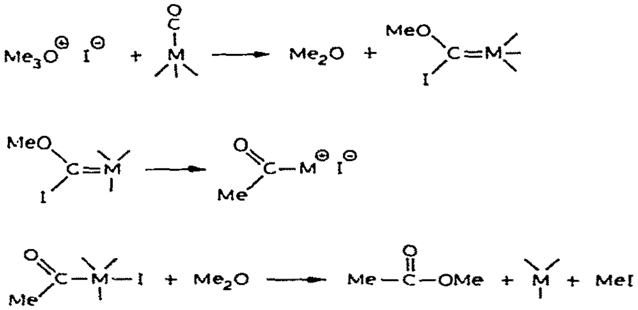
These reactions were attributed to acid ether cleavage by hydrido cobalt carbonyl (p$K_a \sim 1$) formed in situ. The dimethylether cleavage in the Halcon methyl acetate process may proceed analogously.

The mechanism of the Halcon process is unclear and two possibilities are given (Scheme 6); an intermolecular reaction between acyl iodide and dimethylether; methyl acetate may be carbonylated by the same route.

Scheme 7 shows the classical oxonium attack on a metal carbonyl followed by a 1,2-rearrangement.



SCHEME 6



SCHEME 7

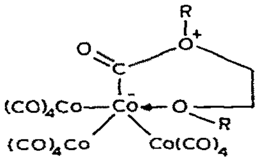
Acyl iodide and methyl acetate react to produce acetic anhydride and methyl iodide and it is clear that the acyl moiety is an intermediate in methyl iodide or iodine promoted reactions [44a]. Pyridine derivatives catalyse organic acylation reactions and Halcon carbonylations.

Methyl iodide promoted reactions are exceedingly corrosive since HI (a very strong acid) may be formed by promoter decomposition or reaction with hydrogen gas or methanol.

(ii) Non-promoted reactions

The OH group oxygen atoms in methoxyethanol are evidently active towards coordination to metals (eqn. (15), Scheme 13) and the production of bis(methoxyethoxy)methane under syngas with methoxyethanol solvent may be viewed as an oxidative coupling of two alcohols in an Ube-type reaction where the alcohol hydrogen is used in hydrogenation, or, the etherification of liberated formaldehyde.

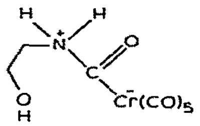
More emphatically the reactions of syngas in glymes and hydroxy glymes using $Co_2(CO)_8$ as a catalyst *without* promotion yield crystalline, but very unstable complexes, probably of formula(e) which reverts to $Co_4(CO)_{12}$ when



R = H or alkyl

(e)

washed with non-glyme solvents or on standing. Similarly, $Cr(CO)_6$ in ethanolamine under syngas yields pale yellow unstable oily crystals. The



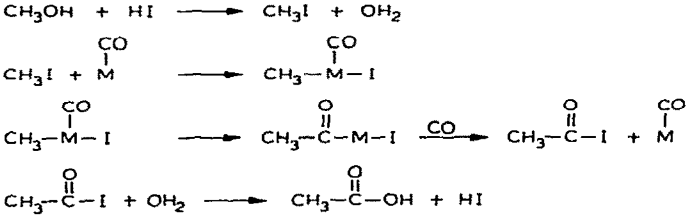
(f)

infrared spectra of this material supports the structure (f), again, these quickly revert to $Cr(CO)_6$ and ethanolamine on standing [45,46].

Thus, in non-promoted and oxidative coupling reactions, we have the unifying theme of oxygen coordination and oxonium ion participation as one possible mechanistic route to carbon monoxide activation.

(iii) Homologation reactions

There is obviously a special mechanism for homologation reactions and conversion of methanol to acetic acid involving displacement of H_2O by HI in a most likely preliminary step (Schemes 8–10).



$$CH_3OH + HI \longrightarrow CH_3I + OH_2$$

$$CH_3I + \overset{\overset{\large CO}{|}}{M} \longrightarrow CH_3{-}\overset{\overset{\large CO}{|}}{M}{-}I$$

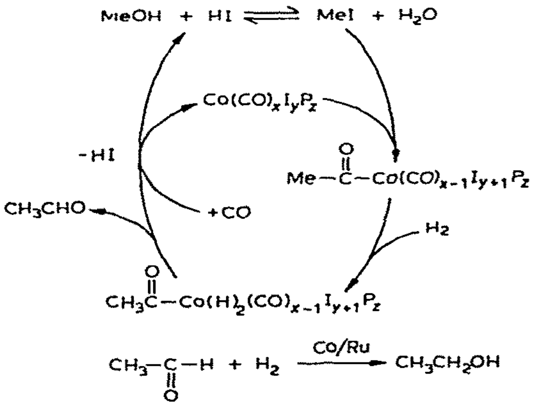
$$CH_3{-}\overset{\overset{\large CO}{|}}{M}{-}I \longrightarrow CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}M{-}I \xrightarrow{CO} CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}I + \overset{\overset{\large CO}{|}}{M}$$

$$CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}I + OH_2 \longrightarrow CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}OH + HI$$

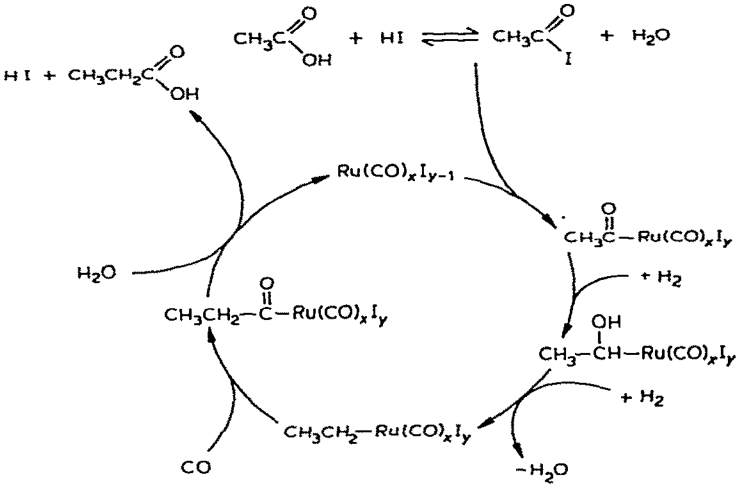
SCHEME 8

The methanol homologation reaction is perhaps the most studied of all hydrocarbonylation reactions; ethanol and acetaldehyde are the major products. Cobalt and ruthenium are the major catalysts, and iodine/iodide is used as promoter; the dual role of phosphine as catalyst stabilizer-promoter is little understood. A basic mechanism is given in Scheme 9.

Acetaldehyde is very reactive and if it is required as a product has to be removed from the reaction zone. It is presumed that ethanol is produced from acetaldehyde hydrogenation.



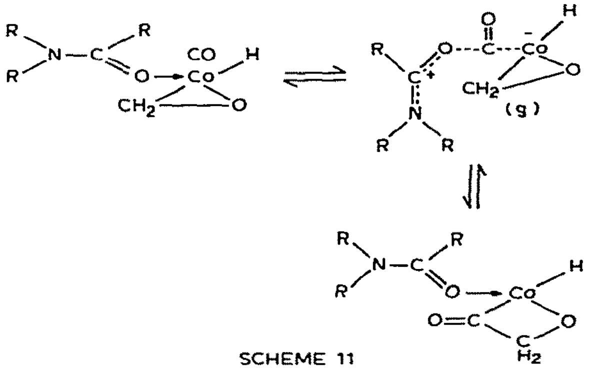
SCHEME 9



SCHEME 10

A similar mechanism for acid homologation with ruthenium catalysts promoted by methyl iodide has been proposed (Scheme 10) [45a].

The hydrocarbonylation of formaldehyde using a rhodium or cobalt catalyst [12,13] is promoted by dimethylformamide, no formates are formed and carbonyl insertion in a metal–carbon bond is proposed. It is possible with amide promoters that the precursor to formaldehyde carbonylation is (g) in Scheme 11, or that the promoter just controls the acidity of the reaction mixture.



SCHEME 11

Amide activators* are particularly interesting; although not useful for all reactions they activate two of the fastest carbonylation processes yet discovered. Those of the Ajinomoto hydrocarbonylation of formaldehyde [13] and the Rhone Poulenc carbonylation of methanol to acetic acid [51]. The Rhone Poulenc process uses N-methyl pyrrolidone (Scheme 12).

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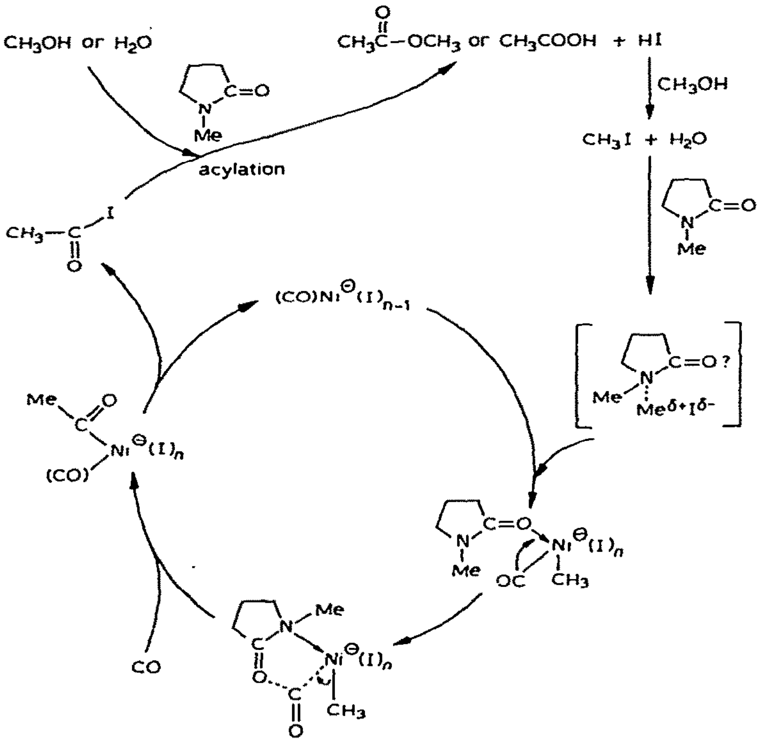
* Note added in proof. A method has been disclosed for the production of acetaldehyde and ethanol from syngas using a ruthenium halide catalyst and an amide activator (U.K. Patent 2074164A, 1981).



SCHEME 12
Carbonylation of methanol using a nickel catalyst. Possible direct roles of *N*-methyl pyrrolidone as solvent-activator.

(iv) Activators in homogeneous carbonylation and hydrocarbonylation reactions

The term activator is used to describe a substance which aids either the selectivity or rate of catalytic reaction. It is not necessarily part of the catalytic cycle and may act in a purely physical chemical way, for instance changing the dielectric constant of the solvent system or controlling the acidity of the reaction medium. Some activators promote secondary catalytic cycles where no metals are involved.

Reactions involving methanol as a feedstock (carbonylations, hydrocarbonylations) are uniformly accelerated by iodine as I_2, methyl iodide, tetraalkyl ammonium, phosphonium or alkali metal iodides. The role of iodine in forming a strong acid (HI) with hydrogen and thus promoting the formation of methyl iodide from methanol is well known. Carbonylation of methyl iodide produces acyl iodide by (1) oxidative addition of methyl iodide to a metal centre, (2) methyl migration to a bound CO ligand and (3) reductive elimination of acyl iodide. Acylation of methanol, water or methylacetate produces methyl acetate, acetic acid or acetic anhydride. All these reactions are catalysed by acylation catalysts such as substituted pyridines. Iodide ion stabilizes many Group VIII metal carbonyl halide anions and it is thus believed to be directly involved in catalytic cycles involving such anions.

The route to acetaldehyde from methanol is a little more complex than a simple organic acylation and involves the competing and selective hydrogenation of a metal bound acyl moiety in the presence of side reactions leading to acetates. Steps to eliminate the acylation of the feedstock lead to high acetaldehyde yields.

The accepted mechanism for the formation of an acyl metal moiety is the intramolecular migration of a methyl group to a bound carbonyl ligand. Acyl formation is probably independent of carbon monoxide pressure above a minimum required to stabilize and reform the catalyst at the temperature of reaction (150–250°C) and the rate steps in the $C_1 \rightarrow C_2$ reactions discussed probably involve the re-formation of methyl iodide. The Halcon carbonylation reactions are roughly independent of CO pressure, but the Rhone Poulenc carbonylation maximizes at about 50 bar partial pressure CO. Nickel tetracarbonyl which is very volatile, may be formed at high CO pressures thus reducing the catalytic activity of the systems.

Tin has long been known [52] to promote carbonylation reactions but its exact role is obscure. Certainly, the alkyl and halogen exchange and oxidative addition reactions of tin halides may be involved; the SnI_3^- ion may act as a ligand.

Water is also known to promote carbonylations of ethers and alcohols; again, its exact role is obscure.

F. SUMMARY OF MECHANISMS

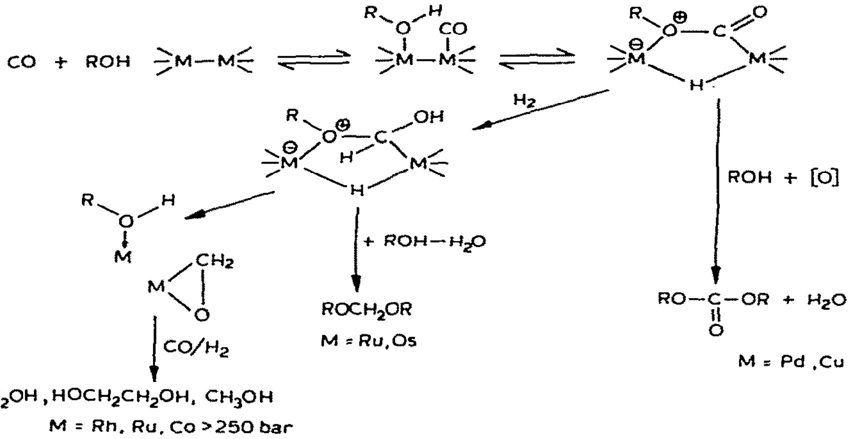
The mechanism of hydrogenation or activation of carbon monoxide for metal catalysed reactions may thus be defined in four ways:

(a) For high pressure (>300 bar) non-promoted reactions a formyl type activation of CO is possible.

(b) In homologation reactions of alcohols or acids preliminary formation of alkyl or acyl iodide is necessary; this oxidatively adds to a metal centre and the acyl moiety is reduced. Alkyl then migrates to a bound carbonyl and reductive elimination of acyl iodide or aldehyde occurs.

(c) In low pressure (<100 bar) ether cleavage reactions, CO may insert into a metal oxygen bond to produce oxonium centres which subsequently cleave to give products. Oxonium centres may be formed with ethers and strong acids. The Halcon methyl iodide promoted carbonylations of ethers and acetates probably proceed via bound or free acyl iodide attack on the feedstock.

(d) 'Oxidative' carbonylation of alcohols may proceed via CO insertion into a metal oxygen bond of a metal bound alcohol, subsequent loss of hydrogen via (a) water formation or (b) reduction of the bound CO by transfer of the alcohol hydrogen via a simple *β*-shift to the metal and hydrogenation of the ketonic CO. This may be followed by coupling on at least four metals Pd [40], Cu [43], Ru and Os [18]. The reason that the products, oxalates and carbonates are stable is that decarboxylation is not favoured under reaction conditions. As such these products may be viewed as a "half-way" stage in an "alcohol gas shift reaction" (Scheme 13).

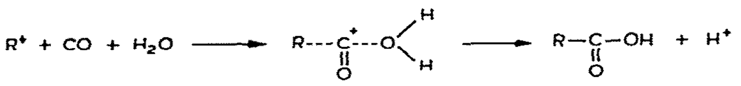


SCHEME 13
Possible routes to carbon monoxide fixation in coordinating alcohol solvents via an oxonium intermediate. Monometallic catalysts are equally feasible (Scheme 4) but bridging hydrogen is *β* to all metal bound atoms for bimetallic systems.

G. NON-METAL CATALYSED CARBONYLATION REACTIONS: THE KOCH REACTION

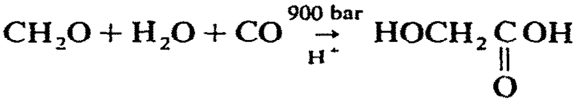
Koch reactions involve the carbonylation of alcohols to carboxylic acids catalysed by mineral acids. They proceed via a carbonium ion intermediate [47].

$$ROH + H^+ \longrightarrow R^+ + H_2O \qquad (35)$$



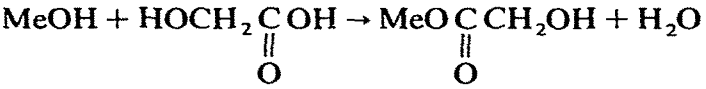
$$R^+ + CO + H_2O \longrightarrow R{-}{-}{-}\overset{+}{C}(=O){-}{-}{-}OH_2 \longrightarrow R{-}C(=O){-}OH + H^+ \qquad (36)$$

Until 1968 the carbonylation of formaldehyde–water mixtures was a major route to ethylene glycol used by DuPont [48].

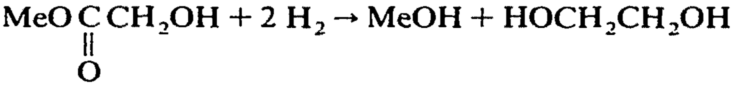


$$CH_2O + H_2O + CO \xrightarrow[H^+]{900\text{ bar}} HOCH_2\underset{\underset{O}{\|}}{C}OH \qquad (37)$$

glycollic acid



$$MeOH + HOCH_2\underset{\underset{O}{\|}}{C}OH \rightarrow MeO\underset{\underset{O}{\|}}{C}CH_2OH + H_2O \qquad (38)$$



$$MeO\underset{\underset{O}{\|}}{C}CH_2OH + 2\,H_2 \rightarrow MeOH + HOCH_2CH_2OH \qquad (39)$$

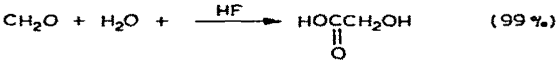
Chevron [49] now run the carbonylation of formaldehyde at 100 bar in aqueous hydrogen fluoride and Mitsubishi [50] use H_3PO_4 as catalyst at 200 bar. Developments in formaldehyde carbonylation will form an alternative to the direct and oxalate routes to ethylene glycol.

H. THE FUTURE OF HOMOGENEOUS SYNGAS CHEMISTRY

It is of interest to note that most of the available processes that function with acceptable pressures and selectivities for commercial use involve carbonylation reactions with iodide promotion. Methanol is the feedstock for all these processes. The Ube oxalic acid processes is a variant in so far as it is an oxycarbonylation reaction. Methanol hydrocarbonylation to acetaldehyde and ethanol can now be achieved with high selectivities (80–90%) but the pressure is too high (150–250 bar) to be of use commercially at present.

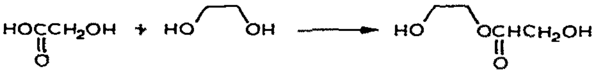
Direct glycol synthesis suffers from selectivity problems and no promoters are known which accelerate the rate of formation fast enough, at present, to make this process acceptable.

The cobalt catalysed hydrocarbonylation of formaldehyde to glycol aldehyde seems attractive but no scale-up plans have been announced which may mean problems in selectivity or development. The Koch route to glycol is energy consuming being a multi-stage process but is highly selective.

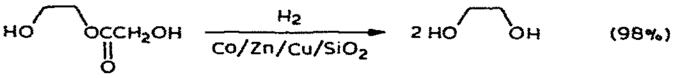


$$CH_2O + H_2O + \xrightarrow{HF} HO\underset{\underset{O}{\|}}{C}CH_2OH \quad (99\%)$$

(40)



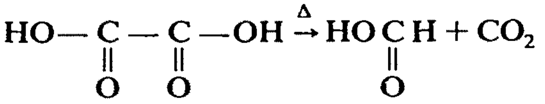
(41)



(42)

Formic acid and hence methyl formate can be made from oxalic acid (eqn.

(43)) (Ube) with CO_2 recycle; this is too expensive to be commercial and a syngas route to formic acid would be useful, although a carbonylation of methanol using a NaOMe catalyst is the present simple route to methyl formate.



$$\mathrm{HO{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}OH \xrightarrow{\Delta} HO\underset{\underset{O}{\|}}{C}H + CO_2} \qquad (43)$$

Methanol can now be homologated to ethanol with CoS and hence "dirty" syngas may be an immediate feedstock [53]. Methanol remains the basic feedstock and the development of a sulphur tolerant methanol catalyst would be extremely interesting, allowing more scope for eventual sulphur removal.

The prospects look brighter for ethanol production via homologation than for direct glycol production from syngas.

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