Synthesis of Two-carbon Compounds by Homogeneous Fischer–Tropsch Type Reactions†

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Summary Carbon monoxide and hydrogen at pressures below 300 atm and temperatures below 200 °C in chelating ethers (glymes) or 2-methoxyethanol containing cobalt and other metal carbonyls react to give ethanol and other oxygenated products; on the basis of reduction using D_2 and study of cobalt complexes, reaction mechanisms are proposed.

The transition metal-catalysed reduction of CO by H_2 in homogeneous solutions to give oxygenated products has usually involved both high temperature (> 200 °C) and pressure (up to several thousand atm),[1–4] although in benzene or dioxan $Co_2(CO)_8$ slowly catalyses reaction at 200 °C and 300 atm.[5]

In polyfunctional ethers (glymes) or 2-methoxyethanol with carbonyls of V, Cr, Mn, Fe, Co, Ru, Rh, and Os as catalyst precursors, reduction occurs below 200 atm and 200 °C. Only Co and Ru give rates approaching industrial interest; for cobalt in diglyme at 200 °C, 150 atm with CO : H_2 = 1 : 1 the conversion rate‡ into ethanol (selectivity *ca.* 80%) is *ca.* $2{\cdot}4 \times 10^{-3}$ (mol CO) [g mol $Co_2(CO)_8$]$^{-1}$ s^{-1} [*cf.* propene hydroformylation[6] at 165 °C, 4×10^{-2} (mol alkene) (g mol Co)$^{-1}$ s^{-1}]. Direct reduction of CO to C_2H_5OH (no methanol is formed) and other products is accompanied by solvent breakdown, the extent being determinable by using D_2 and examining the products by ^{13}C n.m.r. spectroscopy (62·9 MHz; Fourier transform, see Table).

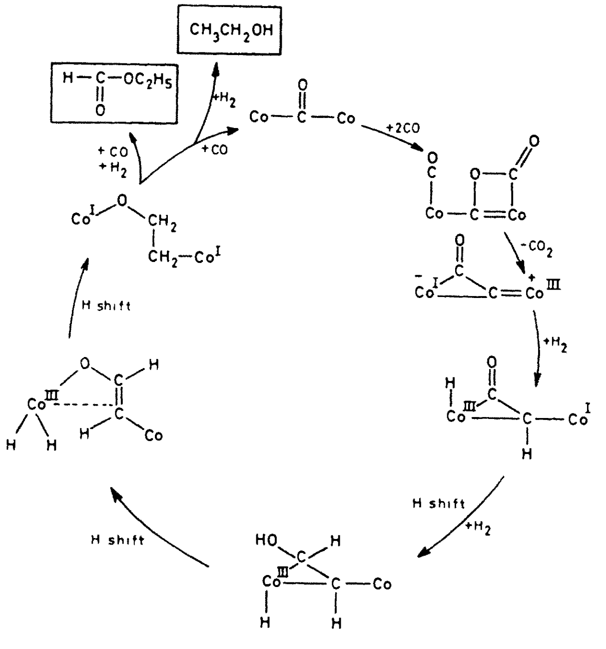

Figure 1. Main steps in the primary cobalt–diglyme cycle at 200 °C to give ethanol and CO_2. Overall stoicheiometry, $3CO + 3H_2 = C_2H_5OH + CO_2$. Co-ordinated solvent and CO omitted from all the Figures.

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† No reprints available.

‡ Rough values only from batch autoclave runs.

Table. Products from CO and D_2 by direct synthesis and solvent breakdown (or secondary build up) using cobalt.[a]

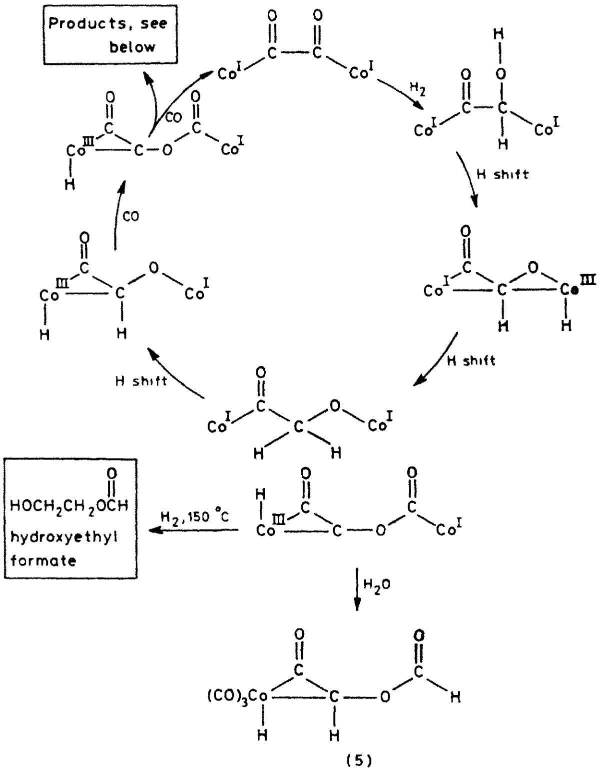
Direct		From solvent	
		Glyme[b] (200 °C)	
Ethanol[e]	(80%)	2-Methoxyethanol	(50%)
Ethyl formate	(6%)	Methyl formate	(20%)
Acetone	(4%)	2-Ethoxyethanol	(10%)
Diethyl ether	(3%)	2-Methoxyethyl formate	(8%)
n-Propanol	(3%)	2-Methoxyethyl *acetate*	(7%)
Isopropanol	(2%)		
		Diglyme[c] (200 °C)	
Ethanol	(80%)	Methyldigol	(80%)
Acetone	(8%)	Methyldigol *acetate*	(7%)
Ethyl formate	(4%)	Methyl formate	(6%)
Diethyl ether	(2%)	Methanol	(2%)
n-Propanol	(2%)	Methyldigol formate	(2%)
Isopropanol	(1%)		
		2-Methoxyethanol[d] (145 °C)	
Ethanol	(60%)	Ethylene glycol	(50%)
Acetone	(6%)	Methyldigol	(15%)
Ethyl formate	(5%)	2-Methoxyethyl formate	(10%)
Diethoxymethane[f]		2-Methoxyethyl *acetate*	(10%)
Triethoxymethane[f]		Bis(2-methoxyethoxy)-*methane*	(5%)
		Ethylene glycol *acetate*	(5%)

[a] Conditions: 150 ml autoclave, 0·7 g of $Co_2(CO)_8$, 60 ml of solvent, initial pressure 130 atm, $CO:D_2(H_2) = 1:1$; cold → hot → cold cycle, 24 h. Groups in italics have been shown to contain deuterium by ^{13}C n.m.r. spectroscopy in CD_3COCD_3. [b] $EtOH:MeOCH_2CH_2OH = 10:1$. [c] $EtOH:MeOCH_2CH_2OCH_2CH_2OH = 1:2$. [d] $EtOH:HOCH_2CH_2OH = 1:1$. [e] $^{13}C\{^1H\}$, Bruker WM-250 at 62·9 MHz: 16 p.p.m., septet, CD_3, quintet CD_2H; 54·5 p.p.m., quintet, CD_2, triplet, CHD; $H:D = 1:4$. [f] Trace.

G.l.c. by Perkin-Elmer F33 and Sigma 1B analyser (+ ionisation detector) on Chromosorb 101 (80—100 mesh; $\frac{1}{8}$ in × 4 m). G.l.c.–m.s. on Perkin-Elmer Sigma 3 + VG Micromass 7070B or Kratos MS 25 *via* jet separator and processed by Kratos DS 50S data system. Relative rates using precursors $Co_2(CO)_8 > Mn_2(CO)_{10} > Cr(CO)_6 > V(CO)_6$.

In Figures 1 and 2 are proposed *initial* catalytic cycles to account for C_2 synthesis at two temperatures. With one exception, these involve well established processes:[7] (a) changes in oxidation state and co-ordination number; (b) oxygen co-ordination to the metal and multidentate behaviour of the solvents (this may be connected with the well known disproportionation reactions of metal carbonyls[8]); (c) CO insertions into a metal–metal bond (or C–C bond formation between two M–CO groups) leading to an M–C(:O)–C(:O)–M moeity; (e) β-hydrogen transfers from both M–C(OH)< and M–O–CH< groups. For the cycle in Figure 1, there is a precedent[9] for carbonylation of a carbene complex and the sequence carbene → ketene → aldehyde/alcohol was proposed.

The following observations are relevant.



(5)

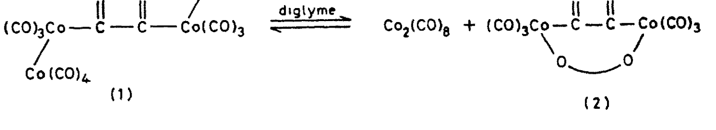
Figure 2. Main steps in the primary cobalt–diglyme cycle below 200 °C. Hydroxyethyl formate, like 2-methoxyethanol (170 °C), may be obtained from solvent breakdown, but as no methoxyethyl formate was obtained this seems unlikely.

(i) The reaction solutions from $Co_2(CO)_8$ in diglyme at 150 °C, $CO:H_2 = 1:1$ (60% selectivity for hydroxyethyl formate formation) are *brown*. At −20 °C these precipitate $Co_2(CO)_8$ leaving a yellow supernate; warming the mixture to −10 °C, gives a red solution from which, at +10 °C, black crystals precipitate. These dissolve on re-cooling whereupon $Co_2(CO)_8$ is again precipitated leaving a yellow supernate. Several cycles cause irreversible loss of CO and formation of $\{(diglyme)_nCo[Co(CO)_4]_3\}$. The black crystals change rapidly, especially if washed with non-glyme solvents, to $Co_4(CO)_{12}$ and $[(diglyme)_2Co]^{2+}[Co_6(CO)_{15}]^{2-}$. Similar behaviour obtains in 2-methoxyethanol.

We propose the black compound to be (**1**), which is in equilibrium (equation 1) with $Co_2(CO)_8$ and (**2**), which is unisolable, but which we suggest also has Co–C(:O)–C(:O)–Co groups and is solvated by diglyme.

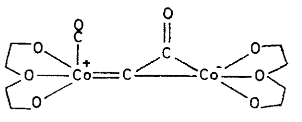
(ii) Under 100 atm of CO in diglyme at 200 °C, $Co_2(CO)_8$ forms insoluble cobalt carbide and an unstable yellow oil (no evidence for diglyme cleavage) identical with that found in catalyst solutions that have made ethanol (200 °C; $CO:H_2 = 1:1$). The oil has i.r. bands at 2080 and 1800 cm^{-1} and we propose that it has the carbenoid structure (**3**) and arises from (**2**) by action of CO.

(iii) The rate using $CO:H_2 = 1·5:1$ with $Co_2(CO)_8$ in diglyme at 160 °C is notably slower than for a 1:1 gas mixture. The components boiling below 160 °C are yellow

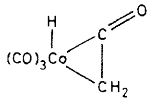


$$\underset{\displaystyle Co(CO)_4}{(CO)_3Co}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle Co(CO)_4}{Co(CO)_3} \xrightleftharpoons{\text{diglyme}} Co_2(CO)_8 + (CO)_3Co{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}Co(CO)_3 \qquad (1)$$

(1) (2)



(3)



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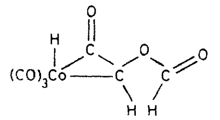

(5)

and include acetaldehyde, ethyl formate, hydroxyethyl formate, and methyl formate Addition of water at 0 °C causes evolution of small quantities (sufficient only for gas-phase i r study) of a yellow gas and methanol The gas is a mixture of two major types of compound, the ratio of which depends on the autoclave reaction period and amount of water added Type (*A*), stable for days, has bands at 2010 (ν_{Co-H}), 2040, 2120 (ν_{Co-Co}), 1820 (a cyclopropanone group[10]), and 1740 [$\nu_{OC(O)H}$] cm^{-1}, consistent with a mixture of (**4**) and (**5**) (formally Co^{III}) Hydrolysis with D_2O produced disappearance of the 2010 cm^{-1} band Compound (**4**) is stable for >3 days, whereas (**5**) decomposes giving CO_2 Type (*B*) has bands at 2010, 2030, 2050, and 1740 cm^{-1} and readily decomposes giving acetone

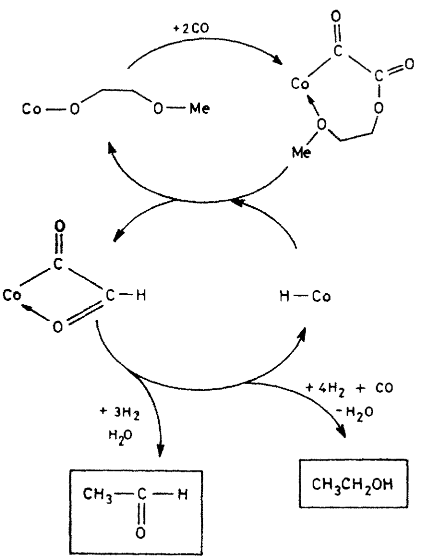

FIGURE 3 Formation of acetaldehyde and ethanol at 130 °C by CO insertion into metal–oxygen bond in 2-methoxyethanol

(iv) Catalyst solutions of $Co_2(CO)_8$ in diglyme, CO : H_2 = 1 : 1 that have operated between 120 and 180 °C always show i r bands assignable to (**1**), $Co_2(CO)_8$, and {(diglyme)$_n$-Co[Co(CO)$_4$]$_3$} and are red-brown Operation at 200 °C gives yellow solutions which, immediately after the reaction, have no bridging or terminal metal carbon monoxide bands [11] From an aged solution, the oil (**3**), was obtained

(v) CO_2 and H_2O are formed as side products, between 150 and 200 °C

The formation of hydroxy-compounds in slow primary cycles must be expected to lead to secondary cycles (Figures 3 and 4) in which alkoxo-groups are involved Such groups will necessarily be present initially in 2-methoxyethanol solutions[11] and can also be derived by breakdown of glyme ethers, especially at the lower temperatures Carbon monoxide insertions into alkoxo-complexes followed by reduction provide likely fast secondary routes to acetaldehyde,§ ethanol, and acetates At *ca* 150 °C and below, HCo-(CO)$_4$ is detected when autoclaves are opened and is probably responsible for ether cleavage

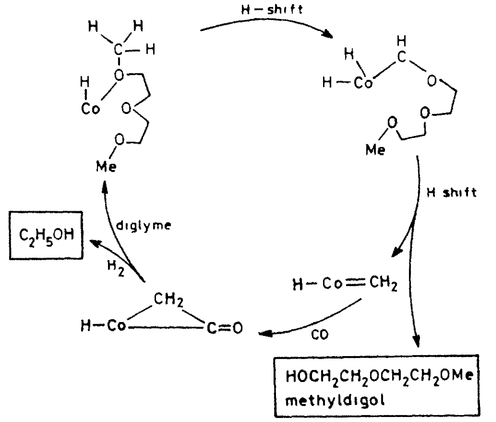

FIGURE 4 Pathway for breakdown of diglyme at 120—150 °C leading to ethanol and methyl digol

Owing to facile β-hydride shifts and CO insertions into M–O bonds, the selective synthesis of ethylene glycol at low temperatures and pressures is difficult, but decarbonylation of hydroxyethyl formate (a major product) or CH_2 extrusion from 2-methoxyethanol will generate glycol ¶

(*Received*, 18*th July* 1980, *Com* 781)

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§ $(CO)_4$Co–C(O)–C(. O)–OCH_2CH_2OMe, which we have synthesised (*cf* J A Gladysz and J S Selover, *Tetrahedron Lett* , 1978, 319) gives acetaldehyde and 2-methoxyethanol (1 : 1) with H_2 (5 atm)

¶ In 2-methoxyethanol up to 40% of the product can be glycol derived in part from the solvent

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