Synthesis of Methanol and Derived Compounds by Homogeneous Fischer–Tropsch Type Reactions†

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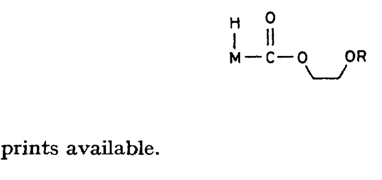
Summary Reduction of CO by H_2 using carbonyls of Fe, Ru, and Os in 2-methoxyethanol below 200 °C and 200 atm gives dimethyl ether and diethyl ether (Fe), methanol and acetone (Ru), and methanol, methyl formate, acetone, and hydroxyethyl formate (Os); catalytic cycles are proposed.

Hydrogenation of CO at 225—275 °C and 1300 atm in tetrahydrofuran using $Ru(acac)_3$ (acacH = acetylacetone) as catalyst precursor gives methanol and methyl formate.[1]

In glyme solvents[2] using $Fe(CO)_5$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ little gas is taken up at 200 °C, 300 atm, but in 2-methoxyethanol appreciable rates, in the order Ru > Os > Fe, are obtained (see Table). Thus, for ruthenium at 180 °C, 180 atm, CO:H_2 = 1:2, methanol is formed with *ca.* 45% selectivity at a conversion rate of about 1·9 × 10^{-3} (mol CO) (g atom Ru)$^{-1}$ s^{-1}. Use of D_2 confirms that CD_3OD is produced by direct reduction of CO, but that there is also, as before,[2] considerable solvent reaction, bis-(2-methoxyethoxy)methane, $(MeOCH_2CH_2O)_2CH_2$, being the major product.

The iron and ruthenium solutions studied immediately after cooling and opening the reaction show *no terminal or bridging CO stretches in the i.r.*, but only a strong band at 1640 cm^{-1} or 1725 cm^{-1}, respectively, which we ascribe to Fe-C(:O)-OR and $\mathrm{Ru^{-}}$-C(:O)-$\overset{+}{\mathrm{O}}$(H)(R) groups. On standing bands due to $Fe(CO)_5$ or $Ru(CO)_5$ and $Ru_3(CO)_{12}$ appear at the expense of the 1640 and 1725 cm^{-1} bands and, simultaneously, what appear to be Fe and Ru alkoxide gels precipitate. Although it was not commented upon, the 1725 cm^{-1} band has been previously observed in Fischer–Tropsch reactions. The product mixture, mostly polymethylene, made over a solid ruthenium oxide catalyst,[3] shows bands due to Ru–CO at 2080 and 2000 cm^{-1} and a strong 1725 cm^{-1} band.

Solutions of $Ru_3(CO)_{12}$ in 2-methoxyethanol under only CO at 100 atm, 170 °C, for 24 h, produce CO_2 and organic products, mostly acetates, but the solution again has a band at 1725 cm^{-1} (no CO stretches) and again gives an alkoxide gel.



(1)

In hydroxy-glymes we then evidently have a reaction (1) similar to the water gas shift reaction[4] and the attack of alcohols on metal carbonyl cations.[5]

The carbonyls of V, Mn, Co, Rh, Ru, and Os all give solutions with a 1725 cm^{-1} band, while Fe and Cr solutions have bands at *ca.* 1640 cm^{-1}; the latter form carbonyls much more slowly. Only for osmium are hydrido-species clearly observed [$H_2Os(CO)_4$ and $H_2Os_2(CO)_8$], but the $^{13}C\{^1H\}$ n.m.r. spectra of the ruthenium catalyst solutions show weak doublet peaks due to CH_3 groups that are coupled to H outside the range of the decoupler (0—10 p.p.m.) while undecoupled spectra have a quartet of doublets.

The reduction of CO by H_2 in all the carbonyl systems depends, we believe, on the stability, under operating conditions in the autoclave, of oxygen co-ordinated com-

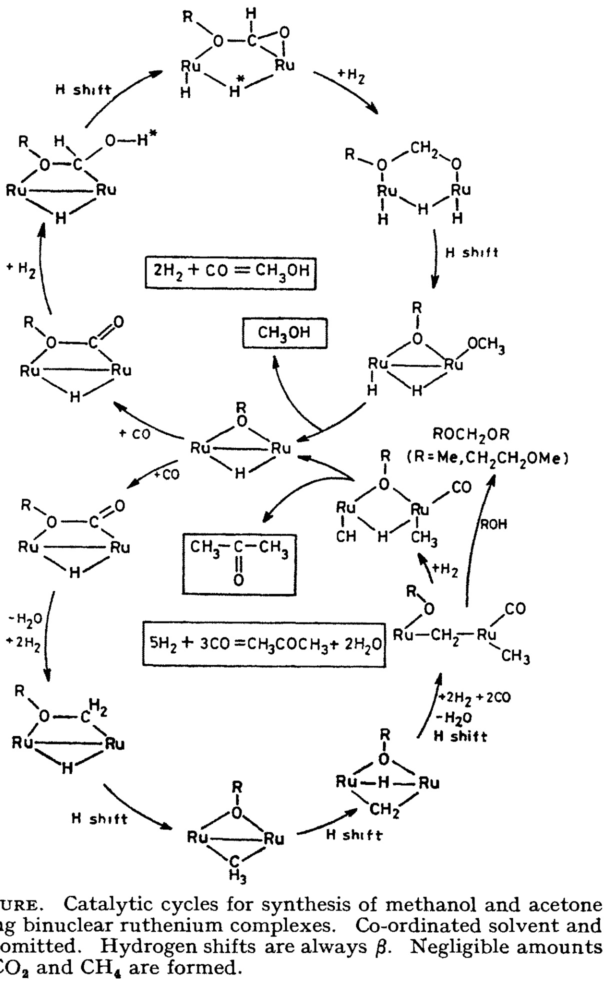


Figure. Catalytic cycles for synthesis of methanol and acetone using binuclear ruthenium complexes. Co-ordinated solvent and CO omitted. Hydrogen shifts are always β. Negligible amounts of CO_2 and CH_4 are formed.

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† No reprints available.

TABLE Catalytic activity of Fe, Ru, and Os carbonyls in 2-methoxyethanol

Metal carbonyl	Time h	CO : H_2 ratio	Pressure /atm	Temp /°C	Conversion[a] (%)	Reduction products (%)[b]
$Fe(CO)_5$	24	1.1	150	160	20	Et_2O (48), Me_2O (36), Me_2CO (6)
$Ru_3(CO)_{12}$	48	1:1 5	180	150	50	MeOH (40), Me_2CO (30), HCO_2Me (5), Me_2O (2)
	48	1.2	180	180	60	MeOH (45), Me_2O (6), HCO_2Me (2), Me_2CO (4)
$Os_3(CO)_{12}$	48	1:1	180	190	40	MeOH (30), Me_2CO (20), HCO_2Me (10), HCO_2Et (6)
	48	1:2	180	190	55	MeOH (40), HCO_2Me (15), Me_2CO (5)

[a] From gas uptake [b] Using D_2 in $MeOCH_2CH_2OD$ (for ruthenium) we obtain CD_3OD ($^{13}C\{^1H\}$ 49 4 p p m , septet)

plexes and this is why glymes and alkoxy-glymes are effective solvents It may be noted that in numerous rapid catalytic systems oxygen co-ordination of the metal is critical[6,7] and indeed, the most active Fischer–Tropsch heterogeneous catalysts are oxide systems [8]

Two cycles leading respectively to methanol and acetone are shown (Figure), although binuclear species are used, similar cycles with mononuclear species can be devised

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