

¹⁴C-Tracer Studies in the Homogeneous Rhodium-catalysed Conversion of Carbon Monoxide and Hydrogen into Methanol and Ethylene Glycol

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¹⁴C-Tracer studies show that methanol and ethylene glycol are primary products of the homogeneous rhodium-catalysed conversion of CO–H₂ mixtures, are not solvent derived, and do not undergo secondary transformation under the reaction conditions; (CH₂O)_x appears to be converted into a common reaction intermediate.

With the recent upsurge of interest in catalysed conversions of CO and H₂, considerable effort is being directed towards the understanding of basic reaction pathways. Hydrocarbon formation over heterogeneous Fischer–Tropsch type catalysts

has received the most attention.¹ Less is known about the synthesis of oxygen-containing species with homogeneous catalysts of which the direct synthesis of ethylene glycol, presently produced in a multistep procedure from crude oil,

Table 1. Rhodium catalysed conversion of CO-H₂ in the presence of ¹⁴CH₃OH, (¹⁴CH₂OH)₂, or (¹⁴CH₂O)_x.^a

Run	Rh conc. g dm ⁻³	¹⁴ C added as	Other additives	Activity balance (%)	¹⁴ C recovered in (%)	Rate (mol dm ⁻³ h ⁻¹)	
						CH ₃ OH	(CH ₂ OH) ₂
1	0.03	CH ₃ OH ^b	—	96.5 ± 2.6	CH ₃ OH only	0.33	0.52
2	0.04	(CH ₂ OH) ₂ ^b	—	99.5 ± 1.0	(CH ₂ OH) ₂ only	0.39	0.62
3	0.04	(CH ₂ OH) ₂ ^b	(CH ₂ OH) ₂ 4.28 g	97.8 ± 1.5	(CH ₂ OH) ₂ only	0.36	0.48 ^f
4	0.04	(CH ₂ O) _x ^c	—	92.5 ± 3	gases ^d (2.2) CH ₃ OH (17) (CH ₂ OH) ₂ (60) Others ^e (8)	0.38	0.56

^a Conditions: Rh₄(CO)₁₂ in *N*-methylpyrrolidin-2-one-tetraethylene glycol, dimethyl ether (1:4) 50 cm³, 850 ± 20 bar, 1:1 H₂-CO, 220 °C. ^b 300 to 400 μCi per run. ^c 233 ± 2 μCi. ^d As MeOH and MeCHO not as CO or CO₂. ^e Principally MeCHO, EtOH, HOCH₂CHOCHO, HCO₂CH₂CH₂OCHO, and HOCH₂CHOCH₂CH₂O. ^f Does not include glycol added at start of run.

is a particularly attractive target.³ It has been generally assumed that methanol and ethylene glycol, the major products of the rhodium-catalysed reaction, are primary reaction products wholly derived from CO and H₂ although this has not been demonstrated unequivocally. More is known of the pathways for oxygenate synthesis with the less active homogeneous cobalt catalysts³ but there was until very recently considerable controversy over the origins, from CO-H₂ or *via* solvent breakdown, of several of the reaction products.[†]

We now show for the rhodium-catalysed reaction using ¹⁴C-tracer techniques that methanol and ethylene glycol are wholly CO-H₂-derived and are not otherwise transformed under reaction conditions, and that formaldehyde is readily incorporated into a typical spectrum of reaction products, most plausibly *via* a common intermediate. To our knowledge, this is the first example of the use of ¹⁴C-tracer experiments with reactions of this type.

The results recorded in Table 1 show that labelled methanol and ethylene glycol are not transformed under reaction conditions. The activity balances are excellent and no other labelled products were detected. Thus, both methanol and ethylene glycol are confirmed as primary reaction products. Methanol does not undergo homologation to ethylene glycol or, more plausibly, to ethanol,⁵ one of the minor reaction products. The third run in Table 1 in the presence of additional unlabelled ethylene glycol is particularly revealing. It has been reported⁶ that the build-up of ethylene glycol and glycerol in the reaction mixture leads to a decrease in the rate of production of ethylene glycol. Ethylene glycol was reported to be 'destroyed' by further transformation. This run does show the reduced rate of production of ethylene glycol but clearly demonstrates that this is not a consequence of secondary reactions. We have separately confirmed this inhibition effect and have shown that increasing amounts (to *ca.* 15% w/v) of ethylene glycol lead to a decrease in production of ethylene glycol but not methanol; production of ethylene glycol was not adversely affected, however, on addition of methanol to similar levels.⁷

A reaction in the presence of ¹⁴CO is recorded in Table 2. In this run the pressure was not held steady *via* regular top-ups but was allowed to fall progressively from a higher initial value. This ensured that the specific activity of the gas did not alter during the run. Ignoring ¹⁴C:¹²C kinetic isotope effects, which the available literature suggests are small,⁸ it can be seen that the specific activities per carbon atom of the CO,

Table 2. Rhodium catalysed conversion of ¹⁴CO-H₂.^a

	Yield (g)	Specific activity (μCi mmol ⁻¹)
CO	—	0.355
CH ₃ OH	1.03	0.334
(CH ₂ OH) ₂	2.52	0.69

^a Conditions: as Table 1 but without pressure top-up; initial pressure 1050 bar, final pressure 800 bar.

methanol, and ethylene glycol are within experimental error identical. Thus, with rhodium (*cf.* † and ref. 4) breakdown of the glycol ether solvent is not a significant source of the methanol and glycol products.

Finally, we investigated the fate of formaldehyde, added as paraformaldehyde, under reaction conditions (Table 1, run 4). The role of formaldehyde, either co-ordinated or free in solution, as a reaction intermediate is still a matter of speculation.^{3a,c,9} It is clear that its formation from CO-H₂ mixtures is thermodynamically unfavourable^{3a} and, while it cannot be a significant reaction product, it could be an important transient intermediate. The very sensitive radiotracer method is ideally suited to monitoring the fate of formaldehyde since it requires the addition of only minute quantities of material which should not perturb the reaction system.

The results for run 4 (Table 1) show that paraformaldehyde is fully converted (2 h) into a mixture of products typical of that for the rhodium-catalysed conversion of CO-H₂. The presence of 2-hydroxymethyl-1,3-dioxolan (labelled) and 1,3-dioxolan (*unlabelled*) in the products lends support to a pathway involving formaldehyde as a precursor of methanol and glycolaldehyde which in turn is a precursor of glycol and higher polyols. The occurrence of the label in the acetal of glycolaldehyde but not in that of formaldehyde suggests that the latter is more labile than the former and that co-ordinated rather than free aldehydes are the more important reaction intermediates. These acetals are most likely produced in a kinetically insignificant side reaction. Interestingly, the ethylene glycol:methanol molar ratio from ¹⁴CH₂O is over twice that for the overall reaction (*ca.* 3.5 *vs.* 1.5), assuming one ¹⁴C per glycol. This could be taken as evidence for an alternative route to glycol *via* (formal) hydrodimerisation of formaldehyde; or else, these differences in selectivity may relate to the operation of subtly different pathways for the transformation of free (labelled) and co-ordinated (*unlabelled*) formaldehyde.

While these results do not unequivocally establish the position of formaldehyde as a transient intermediate they do indicate that (para)formaldehyde is readily converted into the typical mixture of reaction products most plausibly *via* a common reaction intermediate.

† In T. E. Paxson, C. A. Reilly, and D. R. Holecek, *J. Chem. Soc., Chem. Commun.*, 1981, 618, it is clearly shown that the major product, EtOH, of the cobalt carbonyl-catalysed reaction⁴ is derived from the glyme solvents. The same is true of other reaction products.⁴

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