Hydroformylation of Formaldehyde to give Glycolaldehyde with Halide-promoted $Rh_4(CO)_{12}$

Mario Marchionna and Giuliano Longoni*

Dipartimento di Chimica Inorganica e Metallorganica e Centro del CNR per lo Studio della Sintesi e della Struttura dei Composti dei Metalli di Transizione, via G. Venezian 21, 20133 Milano, Italy

Hydroformylation of paraformaldehyde and 37% aqueous formaldehyde to give glycolaldehyde with selectivity up to *ca.* 90% has been carried out in acetone at 90—140 °C and 100—140 atm of carbon monoxide–hydrogen with halide-promoted $Rh_4(CO)_{12}$ as catalyst precursor.

The hydroformylation of formaldehyde is receiving increasing attention as a potential alternative route to C_2 chemicals from C_1 feedstock.[1—9] The most active and selective catalyst precursors so far reported are rhodium(I) phosphine complexes activated by either basic solvents or additives.[3—5] Basic media are probably needed to generate *in situ* active anionic rhodium species;[4,5] however, an excessively basic solvent or an excess of basic promoter often favours the aldol condensation of formaldehyde and glycolaldehyde to give undesirable high-boiling sugar-like by-products,[4,5] and/or deactivation of

Table 1. Effect of halides ($[NBu_4]^+$ salts) on the hydroformylation of CH_2O catalysed by $Rh_4(CO)_{12}$ in acetone at 110 °C and 135 atm of syngas (CO–H_2, 1 : 1).[a]

			Selectivity/mol.%		
X^-	$X^-:Rh_4(CO)_{12}$	Converted CH_2O/%	MeOH	HCO_2Me	$HOCH_2CHO$
–	0	8.7	88.5	—	11.5
F^-	2	10.8	82.8	12.3	4.9
Cl^-	2	70.5	23.0	2.4	74.6
$Cl^{-\,b}$	2	77.8	23.3	2.7	74.0[c]
Br^-	2	21.4	56.0	13.7	30.3
I^-	2	29.2	32.6	4.1	63.3

[a] [Rh] = 2 × 10^{-2} M, [CH_2O] = 2 M (introduced as paraformaldehyde), t = 2 h; the amount of dimethoxymethane formed is included in the methanol figure. Analytical results were obtained following the method described elsewhere (ref. 8). [b] As (a) with the following changes: T = 140 °C, [CH_2O] = 2.9 M (introduced as 37% aqueous formaldehyde). [c] Including *ca.* 1.6% of ethylene glycol.

Table 2. Effect of the molar ratio of Cl^- to $Rh_4(CO)_{12}$ on the hydroformylation of paraformaldehyde in acetone {Cl^- introduced as $[N(PPh_3)_2]^+$ salt, T = 110 °C, $P(CO + H_2)$ = 125 atm, $CO:H_2$ = 1:1}.[a]

	Converted	Selectivity/mol.%		
$Cl^-:Rh_4(CO)_{12}$	CH_2O/%	MeOH	HCO_2Me	$HOCH_2CHO$
0.5	13.0	86.5	—	13.5
1.0	15.3	83.1	—	16.9
1.5	43.1	12.9	5.0	82.1
2.0	71.0	18.9	4.9	76.2
2.5	67.0	28.8	3.9	67.3
3.0	73.4	47.6	2.3	50.1
5.0	85.5	64.4	1.7	33.9

[a] As in Table 1.

the catalyst because of its progressive reduction to species which are too low valent to participate in the catalytic cycle.[6,7] Deactivation of the rhodium catalysts involving phosphines as ancillary ligands[8] may also occur because of the oxidative addition of phosphine to the metal centre.[10] Also, most of the catalytic systems reported so far are only effective in the hydroformylation of paraformaldehyde,[1—8] and only one has shown a comparable ability in catalysing the hydroformylation of the less expensive aqueous formaldehyde.[9]

We have found that a catalytic system involving $Rh_4(CO)_{12}$ as precursor and halides as promoters is effective in the temperature range 90—140 °C and the pressure range 100—140 atm of syngas (CO–H_2, 1:1) in the hydroformylation to give glycolaldehyde of both paraformaldehyde and 37% aqueous formaldehyde in several common organic solvents, *e.g.* acetone. The promotion ability of halides (Table 1) follows the trend $Cl > I > Br > F$, in terms of both activity and selectivity, which is in keeping with the trend recently observed in the direct hydrogenation of CO catalysed by halide-promoted $Ru_3(CO)_{12}$.[11] Onium, *e.g.* $[NBu_4]^+$ and $[PPh_4]^+$, and $[N(PPh_3)_2]^+$ chlorides give rise to comparable activity and selectivity, whereas alkali chlorides, *e.g.* Na^+ and Cs^+, are almost completely ineffective for the hydroformylation of paraformaldehyde in several dry solvents, probably because of their insolubility. However, alkali chlorides become almost as effective as onium chlorides on addition of water, and/or in the hydroformylation of aqueous formaldehyde.

The effect of the Cl^- to $Rh_4(CO)_{12}$ molar ratio on activity and selectivity in the catalysed hydroformylation of paraformaldehyde is shown in Table 2. A sharp increase in activity and selectivity occurs on increasing this ratio up to *ca.* 1.5—2:1, whereas ratios above 2.5:1 appear to be detrimental to the selectivity. Spectroscopic monitoring of the depressurized catalytic solutions unequivocally indicates that a progressive transformation of the precursors, following the known equilibria (1) and (2),[12,13] occurs in all the experiments.

$$3\,Rh_4(CO)_{12} + 4\,X^- \rightleftharpoons 2\,[Rh(CO)_2X_2]^- + 2\,[Rh_5(CO)_{15}]^- + 2\,CO \qquad (1)$$

$$[Rh_5(CO)_{15}]^- + X^- \rightleftharpoons [Rh_5(CO)_{14}X]^{2-} + CO \qquad (2)$$

On using bulky onium counterions, *e.g.* $[N(PPh_3)_2]^+$, addition of water in excess to the depressurized reaction solutions and evaporation *in vacuo* to remove acetone and volatile products leads to a solid mixture {mainly comprising $[Rh(CO)_2Cl_2]^-$, $[Rh_5(CO)_{15}]^-$, and Cl^- salts}, which on subsequent addition of acetone, CH_2O, and pressurization catalyses the title reaction with comparable activity and selectivity. Specific experiments show that none of the preformed salts involved in equations (1) and (2), taken alone, is a catalyst as effective as the chloride-promoted $Rh_4(CO)_{12}$ system. For instance, $[N(PPh_3)_2][Rh(CO)_2Cl_2]$ leads to selective hydroformylation (*ca.* 83% in glycolaldehyde) with only one-third of the activity observed with Cl^- and $Rh_4(CO)_{12}$ (2:1);[8] both the activity and selectivity are greatly depressed by addition of onium chlorides. $[N(PPh_3)_2][Rh_5(CO)_{15}]$ induces both very low activity and little selectivity (*ca.* 45%); addition of chloride ions causes a sharp rise of the activity essentially as a result of a sharp enhancement of the hydrogenation reaction of formaldehyde to methanol. Only combinations of preformed $[Rh(CO)_2Cl_2]^-$ and $[Rh_5(CO)_{15}]^-$ salts in the presence of onium chlorides allowed the catalytic behaviour of the chloride-promoted $Rh_4(CO)_{12}$ to be reproduced; optimization of their relative molar ratios (5:1) resulted in a slight improvement of selectivity (*ca.* 90%). The above system, therefore, seems to represent a further example of catalysts in which two co-existing metal species in different oxidation states may complement each other[8,14,15] in the necessary activation steps of H_2, CO, and CH_2O and, as a result, leading to a faster catalytic reaction.

Although this catalytic system with an overall rhodium concentration in the 10^{-3}—10^{-2} M range shows a productivity (mol. of glycolaldehyde l^{-1} h^{-1}) in the 0.7—1.5 range, which is slightly inferior to values shown by the most active catalysts,[3—9] it presents the advantages of (a) not involving 'unstable' ligands,[8] (b) activity in common organic solvents, and (c) enabling hydroformylation of both paraformaldehyde and aqueous formaldehyde to be carried out with little or no formation of high-boiling by-products. In these experiments by-products (other than those given in Tables 1 and 2) were detected in the hydroformylation of paraformaldehyde only at temperatures above 140 °C; those characterized are 4-hydroxybutan-2-one and methyl vinyl ketone derived from condensation of CH_2O with acetone.[8]

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