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RHODIUM-CATALYZED HYDROFORMYLATION OF FORMALDEHYDE IN PYRIDINES

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The use of pyridines as a solvent greatly enhances the catalytic activity of $RhCl(CO)(PPh_3)_2$ for the hydroformylation of formaldehyde. The yield of glycol aldehyde goes up to over 90% under mild conditions. At temperatures above 100 °C, however, the reaction is complicated by the aldol addition of glycol aldehyde yielding straight-chain sugars.

The glycol aldehyde route for the industrial production of ethylene glycol from syngas seems to be most promising,[1)] seeing that the other processes proposed to date[2)] have unconquerable disadvantages concerning product selectivity and reaction conditions. The catalytic hydroformylation of formaldehyde is a critical step in this route, and several studies have been reported in which specific solvents have been utilized to accelerate the hydroformylation.[3-5)] For example, Monsanto group recently found effective solvents such as N,N-dimethylacetamide (DMA)[4)] and tetraglyme containing triethylamine.[5)] However, the reaction rate in the former and the selectivity in the latter are not satisfactory. In this paper we will report that excellent yields of glycol aldehyde under mild conditions can be achieved by the use of pyridines as the solvent.

$$\text{Syngas} \longrightarrow CH_3OH \longrightarrow CH_2O \overset{CO,H_2}{\dashrightarrow} HOCH_2CHO \longrightarrow HOCH_2CH_2OH$$

The experimental procedure is as follows; paraformaldehyde (600 mg, CH_2O=19.1 mmol),[6)] catalyst (0.05 mmol) and solvent (10 ml) were placed in a 54 ml stainless steel autoclave, which was charged with CO and H_2. The mixture was vigorously stirred with a stirring bar and heated at 70 °C. The reaction mixture was analyzed by GC on a Chromosorb 101 column using butanol or ethanol as an internal standard. The by-products such as methyl formate, acetaldehyde, and glycolic acid were formed less than 2% of the total yield in all the experiments. The powdered paraformaldehyde (for electron microscopy, Nakarai Chemicals) with the formaldehyde content of 95.6%[6)] was used in order to minimize the water content in the reaction system. The addition of water or the use of formalin (35 wt%) increased the formation of methanol. Neither trioxane nor methylal was hydroformylated under these conditions.

In the hydroformylation catalyzed by $RhCl(CO)(PPh_3)_2$ (0.1 mmol) under a pressure of 90 atm (H_2/CO=2) at 100 °C for 12 h, the yields of glycol aldehyde in γ-picoline and in N,N-dimethylformamide (DMF) were 26% and 63%, respectively. On the contrary, the gas absorption rate in γ-picoline was remarkably faster than that in DMF. After the former reaction products had been trimethylsilylated with

Table 1. Hydroformylation of Formaldehyde Catalyzed by $RhCl(CO)(PPh_3)_2$

Solvent	Products yield / %		
	$HOCH_2CHO$	$HOCH_2CH_2OH$	CH_3OH
γ-Picoline	49.4 (40.4)	0.3 (0.2)	0.4 (0.3)
γ-Picoline a)	(32.2)	(0.1)	(6.5)
γ-Picoline - H_2O b)	(28.2)	(≈0)	(2.9)
β-Picoline	43.0	0.3	0.2
Pyridine	42.9	0.4	0.2
4-Pentylpyridine	39.7	0.4	0.4
3,5-Diethylpyridine	35.1	0.1	0.1
DMA - Triethylamine (2×10^{-2} M)	14.5	0.4	≈0
Triethylamine	9.4	- c)	0.4
DMSO	7.4	≈0	0.2
DMA	7.3	0.4	≈0
DMF	4.3	≈0	0.1
Benzene - Triethylamine (0.5 M)	1.3	- c)	2.5
Dioxane	0.8	- c)	0.1
Acetone	≈0	≈0	0.1

CO (25 atm), H_2 (25 atm), 3 h. The other conditions are as in the text. Reactions performed for 2 h are indicated in parentheses. a) Formalin (35 wt%) instead of the paraformaldehyde was used. b) H_2O (1.5 ml) was added. c) Not analyzed.

a mixture of $[(CH_3)_3Si]_2NH$ and $(CH_3)_3SiCl$,[7] the GC analysis (on a Silicone SE-30 column) was carried out. The formation of more than twenty non-volatile sugar-like compounds was confirmed. After reduction of the sugar-like compounds with $NaBH_4$, the GC analysis of the trimethylsilylated products as above indicated the presence of straight-chain polyols; glycerol (5%), 1,2,3,4-butanetetrol (32%), 1,2,3,4,5-pentanepentol (10%), and 1,2,3,4,5,6-hexanehexol (5%).[8] It is different from the formose reaction in that the yields of branched isomers[9] such as 2-hydroxymethylglycerol and 3-hydroxymethyl-1,2,3,4,5-pentanepentol were lower than 2%. These facts signify that the low yield in γ-picoline results from the consumption of glycol aldehyde by a base-catalyzed aldol addition reaction. Therefore, mild reaction conditions are necessary to prevent the consumption of glycol aldehyde.

The solvent effects were investigated at a mild temperature of 70 °C. The amounts of glycol aldehyde were approximately corresponding to that of the absorbed gas in all cases. This suggests that the aldol addition reaction is negligible under these conditions. In DMF and DMA, which Monsanto group found as a good solvent, the yields of glycol aldehyde were very poor under these conditions. On the other hand, the use of pyridines greatly enhanced the activity and selectivity of the rhodium catalyst. The analogous solvent effect was also observed in our separated experiments using a halogen-free complex, $RhH(CO)(PPh_3)_3$, (glycol aldehyde yield; 59% and 3% in γ-picoline and DMF respectively under the same conditions as in Table 1). The catalytic activities in triethylamine and

Table 2. Effect of CO and H_2 Partial Pressures on the Reactivity

Pressure/atm			Yield of products / %		
Total	H_2	CO	$HOCH_2CHO$	$HOCH_2CH_2OH$	CH_3OH
25	12.5	12.5	25.8	0.2	0.2
50	12.5	37.5	27.8	0.2	0.2
50	25	25	40.4	0.2	0.3
50	37.5	12.5	45.3	0.1	0.5
75	37.5	37.5	50.9	0.5	0.2
100	50	50	57.1	0.8	0.4
125	62.5	62.5	57.6	1.1	0.2

At 70 °C for 2 h in γ-picoline (10 ml), the other conditions are as in the text.

DMA containing triethylamine were higher than those in non-amine solvents such as DMSO, dioxane, and acetone. These results indicate that amines are necessary for the hydroformylation. The polarity of the solvents might be also one of the factors, because of the low activity in a benzene solution containing triethylamine. This deduction is consistent with the observation that the yields in pyridines possessing large alkyl substituents were relatively low. Such solvent effects are quite different from those on the rhodium-catalyzed hydroformylation of olefins. It is known that the latter reaction is slow both in polar solvents and in the presence of excess pyridines.$^{10)}$

In the rhodium-catalyzed hydroformylation in γ-picoline, the yield of glycol aldehyde increased with pressure up to 100 atm. The increase of H_2 partial pressure resulted in an increase in the yield of glycol aldehyde and did not seriously affect the methanol formation. It is well known in the hydroformylation of olefins that an excessive pressure of CO suppresses the reaction rate.

A preliminary research to attain a maximal yield of glycol aldehyde was carried out by varying the reaction time under 90 atm (H_2/CO = 2). The yield exceeded 90% within 4 h and reached 94.0% in the period of 6 h. At all stages, methanol was formed in yields less than 1.5%. Even if the reaction time was prolonged to 20 h, glycol aldehyde remained still at 83.7%. The facts indicate that the aldol addition reaction

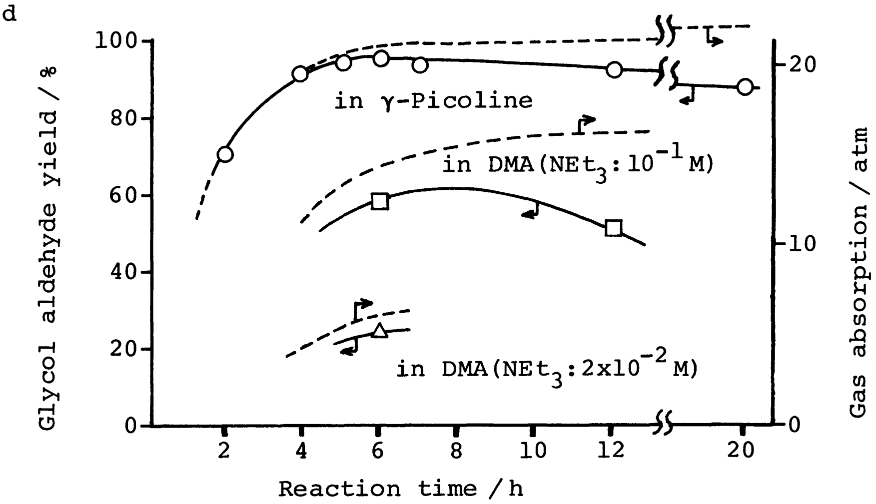

Fig. 1. Hydroformylation of formaldehyde catalyzed by $RhCl(CO)(PPh_3)_2$ (0.1 mmol) in γ-picoline at 70 °C under 90 atm (H_2/CO = 2)

is not serious under these mild conditions. On the other hand, the hydroformylation was slow in a DMA solution containing a small amount of triethylamine at 70 °C. Although the reaction was somewhat promorted by the addition of an excess of triethylamine, the yield was rather low as compared with the gas absorption. Therefore, a strong base like triethylamine should intensify the aldol addition reaction.

The use of pyridines immiscible with water makes it easy to separate the water-soluble products from the pyridines solution of the catalyst by washing the reaction mixture with water. In fact, when 4-pentylpyridine whose mutual solubility to water was 0.28 and 96.3 wt % at 24 °C was used as the solvent, 99.0% of the formed glycol aldehyde from the 78.5% yield could be extracted with 5 ml of water four times. The rhodium content of the aqueous extract was estimated to be less than 2 ppm on the basis of flame emission analysis. Namely, over 99.5% of the rhodium catalyst remained in the separated organic solution. Therefore, it is expected that re-use of the catalyst solution is feasible in principle. These studies are now in progress.

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