

## LIQUID PHASE CO + H<sub>2</sub> REACTIONS IN PRESENCE OF RUTHENIUM CATALYSTS

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Several effects on the hydrogenation of carbon monoxide in propanol in presence of ruthenium catalysts are examined. The homologation reaction is not observed, only propyl formate and propyl acetate are produced with any ruthenium catalyst. The pH-value is an important parameter: in acid media, the yield of propyl formate is noticeably increased indicating different catalytic active species. The addition of cesium salts is also beneficial for formate formation. This is not the case when water is associated with propanol as solvent. Finally, no ethylene glycol is detected. The process is found to be homogeneous and methanol seems to be the precursor of methyl formate.

Изучены различные эффекты, влияющие на гидрирование окиси углерода в пропанол в присутствии рутениевых катализаторов. Реакция гомологирования не наблюдается, в присутствии рутениевого катализатора образуются лишь формиат и ацетат пропила. Важным параметром является значение pH: в кислой среде выход формиата пропила значительно увеличивается, что указывает на различные типы каталитически активных частиц. Добавки солей цезия благоприятствуют образованию формиата. В этом случае вода не ассоциирована с пропанолом, как растворителем. В конечном итоге этиленгликоль не обнаружен. Процесс оказался гомогенным и метанол, по-видимому, является источником метилформиата.

### INTRODUCTION

Homogeneous catalysis by transition metal complexes has obtained increasing attention in the past years, particularly in the Fischer-Tropsch type of hydrogenation of carbon monoxide. The question has been dealt with in recent articles /1-4/.

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Besides cobalt and rhodium catalysts, ruthenium appears to be the most used in catalysis, they are e. g. : homologation /5-6/, hydrogenation /7/, reaction of water with CO /8-10/, direct synthesis of alcohols /11-14/ and diols /15/.

In this article, we investigate the hydrogenation of carbon monoxide in the presence of various ruthenium catalysts (clusters or monometallic compounds) considering several parameters which have hitherto received less attention: the effect of pH, pressure, presence of additives (cesium, benzoate and hydroxide), addition of water.

## EXPERIMENTAL

### 1) Description of a run

The high pressure design has been described elsewhere /18/. The vessel is blown off under an argon stream and filled up with catalyst ( $4 \times 10^{-4}$  mole), solvent (0.04 mole) and additive ( $1 \times 10^{-4}$  mole), then connected to the high pressure line and brought to the desired pressure. After disconnection from the line, the vessel is heated and shaken for a constant reaction time. The pressure drop ( $\Delta P$ ) can be followed continually by a pressure transducer. After cooling overnight, the vessel is discharged by evacuating the gas phase at a very low rate. After full decompression the liquid phase is isolated and analyzed by gas chromatography (GC), as well as the gas phase.

### 2) GC conditions<sup>x</sup>

a) Analysis of CO, CO<sub>2</sub>, H<sub>2</sub>: chromatograph (F and M 720), detection (catharometer), carrier gas (CH<sub>4</sub> 15 ml/min), column (Silicagel: 80-100 mesh, length 5 m, diameter 3, 2 mm), temperature (20 °C - 5 min, then 140 °C - 10 min), injection and detection (150 °C).

b) Analysis of CO<sub>2</sub> and gaseous hydrocarbons: chromatograph (Hewlett-Packard 5700), detection (catharometer), carrier gas (He 30 ml/min), column (Chromosorb

<sup>x</sup>With the collaboration of Mrs. S. Libs and Miss E. Schleiffer

102: 80-100 mesh, length 2 m, diameter 3, 2 mm), programming (from 60 ° to 240 °C - 8 °C/min), injection and detection (200 °C).

c) Analysis of the liquid phase (alcohols, esters): conditions as in b), but column (FFAP, 5% Chromosorb 101: 80-100 mesh, length 4 m).

## RESULTS AND DISCUSSION

### a) Effect of catalysts

The results with some ruthenium catalysts are listed in Table 1.

Following points must be noticed: with RuO<sub>2</sub> wax is produced (42% in weight) in accordance with the results of Pichler /19/. With other catalysts homologation of propanol is not observed, in contrast to earlier patents /11-12/. Only propyl formate and propyl acetate are obtained and this result demonstrates that a chain growing from CO and H<sub>2</sub> is possible. A blank run (propanol + CO) carried out under the same conditions produced only a negligible amount of propyl formate.

### b) Effect of pH

With ruthenium catalysts, the acidity or basicity of the medium seemed to have an important influence on the selectivity: long chain alcohols in alkaline media, solid polymethylens at acidic pH /11-12/. The water-gas shift reaction is also affected by the pH /9/.

When changing the pH from alkaline to acidic we observe a significant increase of the yield for formate (x 4, 3). In this run dehydration of propanol and formation of dipropyl ether occurs. During the reaction the pH decreases (from 11 to 9, 5), the decrease is due either to the formation of CO<sub>2</sub> or to the consumption of the base to give formates. In alkaline media CO<sub>2</sub> is produced in a great quantity (54%), probably in the reaction of water-gas shift reaction catalyzed by Ru /9/. In acidic media, CO<sub>2</sub> is present only in a small amount (< 2%). In any case, no homologation of propanol could be observed.

Table 1

Influence of various ruthenium catalysts (a)

Catalyst	$\Delta P$ (b)	Products (c)		
		propyl formate	propyl acetate	water
$\text{Ru}_3(\text{CO})_{12}$	20	6	0	0
$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$	50	9	1	0
$\text{Ru}(\text{acac})_3$	35	1.3	1.3	0
$\text{RuCl}_2(\text{PPh}_3)_3$	20	0.25	0	0
$\text{RuO}_2$ (d)	120	0.25	0.25	13

(a) T: 205°C, P: 1100 bar, reaction time: 5 h, solvent: PrOH -  
0.04 mol catalyst:  $4 \cdot 10^{-4}$  mol.; CO:H<sub>2</sub> = 1 : 1.

(b) Pressure drop in bar (vessel unheated).

(c) Moles of products for one g-atom of Ru.

(d) Heterogeneous catalysis.

Although mechanistic schemes have been proposed for the water-gas shift reaction in alkaline media, the catalysis at acidic pH-values remains an intriguing point. The results of Table 2 can be explained only by supposing the existence of different catalytic active species at different pH-s.  $\text{H Ru}_3(\text{CO})_{11}$ ,  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  have been identified in alkaline media, while  $\text{H}_2\text{Ru}_6(\text{CO})_{18}$  seems to be in acidic media /9/ /20/.

#### c) Effect of additives

The effect of additives plays an important role in some reactions such as the synthesis of ethylene glycol /17-21/ and the homologation of methanol with Co or Rh as catalysts /16-22/. Table 3 shows our results.

The activity of the catalyst increases seven-fold in the formation of propyl formate. The role of the Cs<sup>+</sup> cation is probably to stabilize the ruthenium active species, as shown with rhodium /21/. Again we observe a decrease of the pH during the reaction.

Table 2

Effect of the pH of the medium (a)

pH		$\Delta P$ (b)	Products (b)			
before	after		Propyl formate	Propyl acetate	Propyl ether	Water
reaction						
5	5	35	1.3	1.3	0	0
11	9.5	30	3.5	2.5	0	0
1	1	90 (c)	15	2.3	20	30

(a) T: 205°C, p: 1100 bar, reaction time: 5 h, solvent: PrOH, 0.04 mol, catalyst: Ru(acac)<sub>3</sub>: 4 × 10<sup>-4</sup> mol, CO:H<sub>2</sub> = 1:1.

(b) see Table 1.

(c) In this run, 1.6% of the products could not be identified.

Table 3

Effect of additives (a)

Additive	pH		$\Delta P$ (b)	Products (b)		
	before	after		propyl formate	propyl acetate	Water
	reaction					
none	11	9.5	30	3.5	2.5	0
CsOH	11.5	7	50	23	1.3	0
(c) BzCs	10.5	9.5	80	26	0.5	0

(a) T: 205°C, P: 1100 bar, reaction time: 5 h, solvent: PrOH: 0.04 mol, catalyst: Ru(acac)<sub>3</sub>: 4 × 10<sup>-4</sup> mol, additive: 1 × 10<sup>-4</sup> mol, CO/H<sub>2</sub>: = 1:1.

(b) see Table 1

(c) Cesium benzoate.

Table 4

Effect of water (a)

pH	$\Delta P$ (b)	Presence of water	Products (b)		
			Propyl formate	Propyl acetate	Propyl ether
1.4	25	yes	3.6	2.6	0.4
1.0	95	no	15	2.3	20
11.4	10	yes	0.2	0.2	0
11.0	30	no	3.5	2.5	0
4.3	10	yes	0.1	0.2	0
5.0	35	no	1.3	1.3	0

(a) T : 205<sup>o</sup> C, P : 1100 bar, reaction time : 5 h, solvent : PrOH +  
+ H<sub>2</sub>O : 0.02 mol + 0.09 mol, catalyst : Ru(acac)<sub>3</sub> : 4 x 10<sup>-4</sup> mol,

CO H<sub>2</sub> = 1 : 1.

(b) see Table 1.

#### d) Effect of water

The effect of partial substitution of PrOH by water at different pH-values is shown in Table 1.

At any pH, the addition of water hinders the formation of formate. It should be pointed out that these results are conflicting with those extracted from a patent /12/, which indicates that the addition of water is favorable for the synthesis of high boiling alcohols.

#### e) Influence of pressure and temperature

As it was impossible to reproduce some results /11-12/ obtained with RuO<sub>2</sub> with homogeneous catalysts, we have tested the activity of Ru(acac)<sub>3</sub> in conditions close to those used for the synthesis of ethylene glycol /17/. The results are listed in Table 5. With increasing pressure and temperature, Ru(acac)<sub>3</sub> dissolved in tetraglyme

Table 5

Hydrocondensation of CO with ruthenium catalysts (a)

Catalyst	P(bar)	T (°C)	ΔP (b)	Solvent
Ru(acac) <sub>3</sub>	1100	205	35	PrOH
Ru(acac) <sub>3</sub>	1700	230	130	PrOH
Ru(acac) <sub>3</sub>	1700	230	110	Tetraglyme
Ru <sub>3</sub> (CO) <sub>12</sub>	1100	205	20	PrOH

Products (b)

	MeOH	MeFt	MeAc	EtAc	PrEt	PrAc	H <sub>2</sub> O
Ru(acac) <sub>3</sub>	0	0	0	0	1.3	1.3	0
Ru(acac) <sub>3</sub>		0	0	0	13.5	2	4
Ru(acac) <sub>3</sub>	3.5	1.8	0.5	0.5	0	0	3
Ru <sub>3</sub> (CO) <sub>12</sub>	0	0	0	0	6	0	0

(a) catalyst :  $4 \times 10^{-4}$  mol, solvent: 0.015 mol, reaction time: 5 h, CO:H<sub>2</sub> = 1:1.

(b) see Table 1. Abbreviations mean, respectively: methanol, methyl formate, methyl acetate, ethyl acetate, propyl formate, propyl acetate.

leads to the synthesis of methanol, methyl formate and acetate. These results are similar to Bradley's results /13-14/ obtained in tetrahydrofuran at a higher temperature (270 °C). The higher pressure associated with a lower temperature allows us to avoid the formation of hydrocarbons, which would occur through a heterogeneous process after the decomposition of the catalyst /23-24/. The IR-characterization of Ru(CO)<sub>5</sub> at the end of the reaction, as well as the absence of methane suggest that the formation of our products is a homogeneous process. With propanol as solvent, only propyl formate and acetate and traces of methanol are obtained. No ethylene glycol could be detected in the reaction products, unlike in a recent patent /15/.

The mechanism of the synthesis remains hypothetical. Would it be a mechanism through chain-growing as suggested by Olivé for the formation of alcohols /25/ where alcohols and esters would be formed through a common reaction species? Or, alternatively, would methanol be a primary product from which the esters would derive or opposite? Only a partial answer can be proposed: in the same reaction conditions as those defined in Table 1 (catalyst Ru(Acac)<sub>3</sub>, the reaction CH<sub>3</sub>OH + CO leads to the formation of 10% methyl formate (on methanol basis), while the reaction MeEt + H<sub>2</sub> gives only CH<sub>4</sub>, CO and traces of CO<sub>2</sub> and H<sub>2</sub>O. Thus methanol appears as a primary product and can produce methyl formate.

The results of the present work draw the attention to an important problem. We described previously /17/ the synthesis of ethylene glycol with rhodium catalysts, but also in the presence of Ru<sub>3</sub>(CO)<sub>12</sub> at high pressure. Since then, two other works /15-26/ reported similar results. However, we never could reproduce the run with Ru<sub>3</sub>(CO)<sub>12</sub> when operating in a vessel, which has not been in contact with any rhodium catalyst. We suspect that in the former run, the formation of ethylene glycol was due to catalysis with metallic sediments of rhodium incrustated on the wall of the vessel (we showed that ethylene glycol is produced with an appreciable yield by rhodium foam).

## CONCLUSIONS

In the present investigation we studied the catalytic activity of some ruthenium compounds for the hydrocondensation of carbon monoxide. Some effects could be shown:

- the effect of pH on the synthesis of formates
- the important influence of the presence of cesium compounds on the activity of the catalyst
- the formation of methanol and methyl formate at higher pressure and temperature without the formation of hydrocarbons
- the absence of ethylene glycol, in contrast with other works.



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