# Hydroformylation and hydroalkylcarbonylation of 3,4-dihydro[2H]pyran catalysed by $Co_2(CO)_8$ under syngas conditions

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Abstract In the cobalt-catalysed hydroformylation of 3,4-dihydro[2H]pyran, the influence of different reaction parameters such as time, pressure, triphenylphosphine addition, catalyst and substrate concentration has been investigated. 2-formyl-tetrahydropyran, tetrahydropyran and a hydroalkylcarbonylation product were the main reaction products. The selectivity towards 2-formyl-tetrahydropyran formation is favoured at constant catalyst and substrate concentration. The coordination of the pyran's oxygen to the cobalt atom seems to be an important intermediate for the formation of 2-formyl-tetrahydropyran. Different substrate or catalyst concentrations promote the formation of other reduced products. The addition of triphenylphosphine to the catalyst leads to a less active species, which decreases the yield and promotes the hydroalkylcarbonylation reaction.

## Introduction

Hydroformylation reactions have been regarded as one of the most important catalytic processes, [1, 2] but only a few reports on the hydroformylation of functionalised cyclic and acyclic alkenes are known [3, 4]. These substrates yield aldehydes that are of interest for the preparation of

P. Sharma · A. Cabrera Instituto de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, Circuito Exterior, Coyoacán, CP 04510 México, DF, México intermediates for the synthesis of fine chemicals [5], natural products or pharmaceuticals [6]. In 1964, Falbe et al. [7] reported  $Co_2(CO)_8$ -catalysed hydroformylation of dihydropyran under very drastic conditions (300 atm CO/H<sub>2</sub>) 1:1 at 190 °C) and obtained 2 hydroxymethyl-tetrahydropyran as a major reaction product along with small quantities of its 3-isomer and tetrahydropyran. Similar results were obtained by Polo and co-workers [8], employing a dinuclear rhodium complex with phosphine, but in this case, both 2- and 3-substituted aldehydes were detected as main products in 2:1 yield. To the best of our knowledge, after these two reports, no information has appeared on the carbonylation of pyrans using either Rh or Co as catalyst. In continuation of our interest in cobaltcatalysed carbonylation reactions [9-11], here we report a systematic study on the influence of different reaction parameters, such as time, pressure, PPh3 addition, catalyst and substrate concentration, on the homogeneous hydroformylation of 3,4-dihydro[2H]pyran, Scheme 1.

## Experimental

Tetrahydrofuran was dried and deoxygenated by distillation under argon from sodium benzophenone ketyl before use.  $Co_2(CO)_8$  was purchased from Strem Chemical Company, PPh<sub>3</sub> from Aldrich, CO and H<sub>2</sub> were from Matheson and used without further purification.

The high-pressure catalytic reactions were carried out in a 80-ml Parr reactor. A typical experiment was performed as follows: a solution of 3,4-dihydro[2H]pyran (1 ml, 10.1 mmol) and  $Co_2(CO)_8$  (0.034 g,  $1.0 \times 10^{-1}$  mmol) in THF (5 ml) was introduced by suction into an evacuated high-pressure reactor described above. Before introducing the mix CO/H<sub>2</sub> at the desired pressure, the system was

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Scheme 1 Different reaction products obtained in the hydroformylation of 3,4dihydro[2H]pyran



purged 2 or 3 times with CO. Then, the reaction vessel was closed, pressurised and heated with stirring at a temperature of 150 °C from 1 to 10 h. At the end of the time, the reactor was cooled (final pressure was 650 psi) and the gases were liberated. The solution was percolated through a column packed with alumina and the resulting yellow solution was analysed on a JEOL JMS-AX505HA GC-MS instrument with a 25 m  $\times$  0.25 mm glass column packed with 5 % phenylsilicone and quantified by GC using hexane as an internal standard in a Hewlett Packard 5890 analyser with a 30 m  $\times$  0.53 mm glass column packed with methylsilicone. The <sup>1</sup>H and <sup>13</sup>C NMR spectra, of the crude products in THF, were recorded on a JEOL 300 MHz spectrometer using (CH<sub>3</sub>)<sub>4</sub>Si as internal reference in CDCl<sub>3</sub> as solvent at 25 °C. The IR spectra were obtained by using a Nicolet FTIR Magna 750 spectrometer.

# **Results and discussion**

These reactions were performed at relatively low pressures, and 2- and 3-formyl-tetrahydropyrans, their corresponding alcohols, tetrahydropyran and bis (2-tetrahydropyranyl)methanol (the hydroalkylcarbonylation product hacp) were obtained. 2-Tetrahydropyranyl tetrahydropyran-2carboxylate was also obtained in a very low yield. The selectivity towards the formation of 2-aldehyde, tetrahydropyran and hacp depends on the experimental conditions (Table 1).

### Effect of time

In order to observe the effect of time on hydroformylation reaction of dihydropyran, experiments were performed at constant syngas pressure, substrate and catalyst concentration at a temperature of 150 °C for 1–10 h. The results are shown in Table 1 and Fig. 1, which indicate a proportional increase in aldehyde, alcohol and hacp yields with time, obtaining 68 % as maximum yield for the total aldehyde with a selectivity of 21:1, (2- to 3-formyl-tetrahydropyran). This high selectivity may be due to the

	% compounds/time (h)					
	1	2	4	6	8	10
Tetrahydropyran	-	1	3	3	4	4
3-formyl-tetrahydropyran	1	2	3	3	3	3
2-formyl-tetrahydropyran	19	39	44	54	60	65
3-hydroxymethyl-tetrahydropyran	_	1	1	2	3	3
2-hydroxymethyl-tetrahydropyran	2	3	5	6	8	10
Hydroalkylcarbonylation product	3	4	6	7	8	10
Ester	-	1	1	2	3	4
Total transformation	25	51	63	77	89	99
Total aldehyde	20	41	47	57	63	68
Total alcohol	2	4	6	8	11	13
Aldehyde selectivity	80	80	75	74	71	69

 $Co_2(CO)_8$  0.1 mmol; 3,4-dihydro-[2H]-pyran 10.1 mmol; THF 5 ml; H<sub>2</sub>/CO 1:1 P = 54.4 atm; temperature 150 °C



Fig. 1 Aldehyde formation as a function of time (1-10 h). Co<sub>2</sub>(CO)<sub>8</sub> 0.1 mmol; 3,4-dihydro[2H]pyran 10.1 mmol; THF 5 ml; H<sub>2</sub>/CO 1:1 pressure 54.4 atm; temperature 150 °C. *Circle* total aldehyde, *diamond* total alcohol and *star* hacp



coordination of pyran's oxygen atom to the cobalt atom bringing the  $\alpha$ -position closer to cobalt, (Scheme 2). Under such conditions, tetrahydropyran, a reduction product, was obtained in a very small amount, <4 %, and this yield is based on the amount of 3,4-dihydro[2H]pyran introduced.

## Effect of catalyst concentration

The effect of catalyst concentration was carried out in the range 0.1–0.5 mmol. The results obtained are given in Fig. 2, which shows that an initial increase in catalyst concentration increases the aldehyde concentration up to 0.2 mmol, after which further increment in the catalyst concentration decreases the aldehyde formation. A similar trend is observed with the alcohol, although it is less pronounced. Moreover, the tetrahydropyran concentration increases significantly and is proportional to the catalyst addition. The formation of tetrahydropyran takes place via an alkyl-metalated intermediate as reported earlier with other non-functionalised alkenes, [12] Scheme 3. Under such conditions, the hacp was not detected.

## Effect of substrate concentration

Figure 3 shows the influence of substrate concentration studied in an interval of 10.1–30.3 mmol. A decrease in the aldehyde formation with the increase in substrate concentration was observed, and an increase in both tetrahydropyran and hacp yields was also noted. Under these experimental conditions, the decrease in aldehyde concentration cannot be explained by its transformation to the corresponding alcohol, as this compound was not detected in a significant amount. On the other hand, the main reaction product was hacp, though under hydroformylation conditions, the formation of diorganyl ketones can be observed using relatively simple olefins, which is in contrary to complex olefins [13, 14]. The hacp was generated from the reductive elimination of the



CO

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CO

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 $^{\circ}CO$ 

CO

Fig. 2 Aldehyde and alkane formation as a function of  $Co_2(CO)_8$  concentration (0.1–0.5 mmol). 3,4-dihydro[2H]pyran 10.1 mmol; THF 5 ml; H<sub>2</sub>/CO 1:1 pressure 54.4 atm; temperature 150 °C, time 10 h. *Circle* total aldehyde, *diamond* total alcohol and *square* tetrahydropyran

acyl-Co and alkyl-Co species formed due to the excess of the substrate. Under the experimental conditions used in this work, it was not possible to detect the carbonyl compound, suggesting that the reduction step of hacp is too fast to isolate the dipyranyl ketone. In these conditions, tetrahydropyran was obtained in appreciable amounts.

## Effect of total pressure

The effect of syngas pressure on the products formation was studied in a range of 27.2–54.4 atm (400–800 psi), and



70

60

20

% yield



10.115.1520.225.2530.3Concentration of sustrate (mmol)Fig. 3 Products formation as a function of substrate concentration(10.1–30.3 mmol).Co2(CO)80.1 mmol; THF 5 ml; H2/CO 1:1pressure 54.4 atm; temperature 150 °C; time 10 h. Circle total

aldehyde, square tetrahydropyran and star hacp

these results are shown in the Fig. 4. It is observed that the total transformation increases with the increasing pressure, for instance from 26 % at 27.2 atm. to 99 % at 54.4 atm. This suggests that catalytic species is more active at elevated pressure, whereas lowering of syngas pressure deactivates it.

## Effect of PPh3 addition

The effect of PPh<sub>3</sub> addition as a ligand with  $Co_2(CO)_8$  in a Co/PPh<sub>3</sub> ratio of 1:2 was studied and the results are shown in the Fig 5. The graph suggests the participation of less active catalytic species in the reaction when phosphine-modified cobalt system is used rather than the unmodified system. It was observed that the reaction proceeds slowly and the aldehyde yield after 11 h is 54 %, which is less

Fig. 4 Aldehyde formation as a function of the pressure (27.2–54.4 atm).  $Co_2(CO)_8$  0.1 mmol; 3,4-dihydro[2H]pyran 10.1 mmol; THF 5 ml; H<sub>2</sub>/CO 1:1 pressure 54.4 atm; temperature 150 °C; time 10 h. *Circle* total aldehyde, *diamond* total alcohol and *star* hacp

Pressure (atm)



Fig. 5 Aldehyde formation with the  $Co_2(CO)_8/PPh_3$  system as a function of time (1–11 h).  $Co_2(CO)_8$  0.1 mmol; PPh<sub>3</sub> 0.2 mmol; 3,4-dihydro [2H]pyran 10.1 mmol; THF 5 ml; H<sub>2</sub>/CO 1:1 pressure 54.4 atm; temperature 150 °C. *Circle* total aldehyde, *diamond* total alcohol and *star* hacp

Fig. 6 a IR spectra of unmodified catalyst. b IR spectra of modified catalyst



than the yield obtained using the unmodified system. Furthermore, the alcohol yield decreases slightly with the modified Co system, and the catalytic species HCo (CO)<sub>3</sub>PPh<sub>3</sub> seems to promote the reaction between mononuclear species in order to increase the hacp yield.

# IR results

The carbonyl vibration frequencies of modified and unmodified catalytic systems were also studied. In the unmodified  $Co_2(CO)_8$ , bands at 2,045, 2,070 and 2,022 cm<sup>-1</sup> were detected, which correspond to the terminal CO group, and a wide band localised between 1,894 and 1,885 cm<sup>-1</sup> indicating the presence of HCo(CO)<sub>4</sub>, similar results were observed earlier also [15]. However, when PPh<sub>3</sub> was added to the

 $Co_2(CO)_8$  solution, the bands observed at 2,045 and between 1,894 and 1,885 cm<sup>-1</sup> disappeared and new bands appeared in the 1,986 and 1,957 cm<sup>-1</sup> regions, indicating the presence of a disubstituted species [16] (Fig. 6).

### Conclusion

Cobalt-catalysed hydroformylation of 3,4-dihydro[2H]pyran was investigated, and the selective formation of the aldehyde, tetrahydropyran and the hacp as a function of the reaction parameters was studied. The coordination of the pyran's oxygen to the cobalt seems to be an important intermediate to the 2-formyl-tetrahydropyran formation. Surprisingly, the generation of the hacp was favoured at high substrate concentration, in spite of the fact that it contains a relatively hindered structure. The active catalytic intermediates appear to be efficient in order promote the hydroalkylcarbonylation reaction. To the best of our knowledge, this is the first systematic study on the hydroformylation of pyran using  $Co_2(CO)_8$  as catalytic system. It is to be mentioned that only a report using Rh has appeared in the early 80's for the hydroformylation of the pyran ring.

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