Hydroformylation versus hydrocarboxylation of cyclohexene under homogeneous WGSR conditions: The study of $Co_2(CO)_8$ diphos/THF–H_2O system

Armando Cabrera [a], Pankaj Sharma [a], Jose Luis Garcia [a], Luis Velasco [a], F. Javier Perez [a], José Luis Arias [b,*], Noe Rosas [a]

[a] *Instituto de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, Circuito Exterior, Coyoacán, 04510 Mexico D.F., Mexico*

[b] *Facultad de Estudios Superiores Cuautitlán, Universidad Nacional Autónoma de México, Cuautitlán Izcalli, Estado de México, Mexico*

Abstract

The catalytic system $Co_2(CO)_8$/diphos/THF–H_2O, an effective catalyst for carbonylation reactions, was studied for simultaneous hydrocarboxylation and hydroformylation of cyclohexene. Using this catalytic system, cyclohexene with CO and H_2O gives cyclohexenecarboxaldehyde and cyclohexenecarboxylic acid as the main reaction products and cyclohexyl-methanol as by-product. The catalytic reaction shows that the hydrocarboxylation/hydroformylation ratio is dependent on water concentration and the reaction temperature. The effects of the other reaction variables such as CO pressure and catalyst concentration were also examined.

1. Introduction

Catalytic hydroformylation and hydrocarboxylation reactions in homogeneous phase have aroused great interest, mainly due to their wide industrial and laboratory use in the production of aldehydes, alcohols and organic acids [1–4]. A convenient method to obtain these compounds is carbonylation of alkenes using the water–gas shift reaction (WGSR) conditions.

Early applications of homogeneous water–gas shift reaction in the hydroformylation of alkenes using $Co_2(CO)_8$ modified with diphos as catalyst were made in polar aprotic solvents such as THF, dioxan, Et_3N, etc., the ratio of linear/branched aldehydes obtained were approximately one [5,6]. Under the same reaction conditions in protic solvents, Murata et al. found the formation of C_4 acids and C_4 alcohols in the hydroformylation of propene [7]. Recently it has been reported that the presence of small amounts of water has an important effect on the alcohol/aldehyde ratio obtained on the hydroformylation of 1-octene using modified cobalt

* Corresponding author. Tel.: +52-6224421; fax: +52-616-2217.

carbonyl $(Co_2(CO)_8/P(^nBu)_3)$ as catalyst under phase transfer conditions [8]. Here we wish to report the catalytic hydroformylation and hydrocarboxylation of cyclohexene under homogeneous water–gas shift reaction conditions with the $Co_2(CO)_8$ diphos/THF–H_2O system as catalytic precursor. We found regioselectivity in aldehyde or acid depending of several variables.

2. Experimental

The solvents and reagents were purified and deoxygenated by distillation under argon from sodium benzophenone ketyl before use. $Co_2(CO)_8$ was purchased from Strem Chemical Company, 1,2-bis(diphenylphosphino)ethane (diphos), from Aldrich, CO was from Matheson and used without further purification. The water was appropriately degassed prior to use.

The high pressure catalytic reactions were carried out in a 300 ml Parr reactor equipped with mechanical stirring and automatic temperature control. A typical experiment was performed as follows: 4.0×10^{-1} mM of the catalyst, 2.0×10^{-1} mM of diphos, water in a range of 60 to 300 mM and 15.0 mM of cyclohexene in THF solution (40 ml) were introduced in the high pressure reactor described above. Before introducing the CO at the desired pressure, the system was purged 2 or 3 times with CO. The reaction vessel was closed, pressurized with CO and heated with stirring at a temperature of 135°C. The reaction products were analyzed on a Hewlett Packard 5895 B GC-MS equipment with a 25 m × 0.3 mm glass column packed with 5% phenylsilicone and compared with pure Aldrich samples, quantified by GC using hexane as an internal standard in a Hewlett Packard 5890 analyzer with a 20 m × 0.2 mm glass column packed with Carbowax 20 M. The ^1H NMR spectra of the isolated compounds were obtained with a Gemini 200 MHz spectrometer using $(CH_3)_4Si$ as internal reference in $CDCl_3$ as solvent at 25°C.

3. Results and discussion

3.1. Effect of water concentration

In order to study the effect of water concentration on the acid/aldehyde ratio in the carbonylation of cyclohexene reaction, experiments were performed at 135°C with varying concentration of water, at constant CO pressure and at constant concentration of cyclohexene and catalyst. The effect was studied in the range of 60 to 300 mM concentration of water. The results reported in Fig. 1 show an increase of aldehyde formation with a maximum yield of 44.0% at 120 mM of water [1]. Further increase of the water concentration results in significantly lower yields of aldehyde.

Fig. 1 also shows that the water concentration has a great effect on the acid/aldehyde distribution. Up to 120 mM of water aldehyde formation is greater in comparison to the acid formation. At higher water concentration acid, formation curve increases with a maximum at 180 mM while the aldehyde yield decreases. At even higher water concentration all the reaction products decrease, this may be due to the formation of inactive $Co^{+2}(H_2O)_n$ species at maximum water concentration [9,10].

3.2. Effect of temperature

This study was carried out by varying the temperature in the range from 110 to 185°C at two different water concentration and at constant concentration of the other reactants. The temperature dependence is illustrated in Figs. 2 and 3.

At 120 mM of water concentration and at 135°C (Fig. 2), we obtain aldehyde, acid and alcohol in 44.0%, 5.5.%, 13.0%, yields, respectively. After this temperature there is a pro-
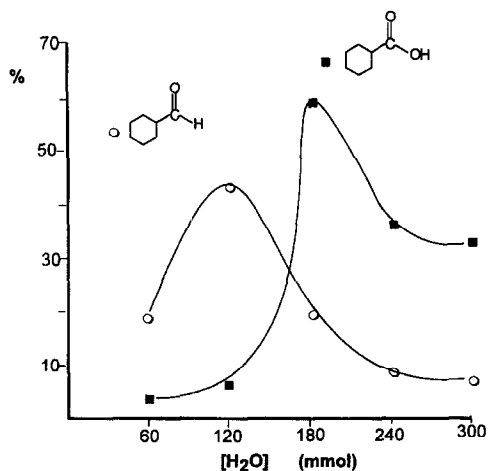

Fig. 1. Effect of the water concentration (0.0 to 300 mmol of H_2O), on the cyclohexene carbonylation: $Co_2(CO)_8$ 0.4 mmol, diphos 0.2 mmol, cyclohexene 9.85 mmol, P_{CO} 34 atm, THF 40 ml, temperature 135°C, reaction time 20 h, aldehyde (O), acid (■).

Fig. 3. Aldehyde/acid formation as a function of temperature (110 to 185°C): 180 mmol of H_2O, $Co_2(CO)_8$, 0.4 mmol, diphos 0.2 mmol, cyclohexene 9.85 mmol, P_{CO} 34 atm, THF 40 ml, reaction time 20 h, aldehyde (O), acid (■), alcohol (⊕).

nounced decrease in the aldehyde formation with the increase of acid and alcohol formation (13.5 and 40.8, respectively, up to 160°C). At higher temperatures there is a decrease of acid and alcohol.

At 180 mM. water concentration a similar pattern was observed for aldehyde and acid (Fig. 3),. The maximum yield of acid (59.6%) was obtained at 135°C. At higher temperatures
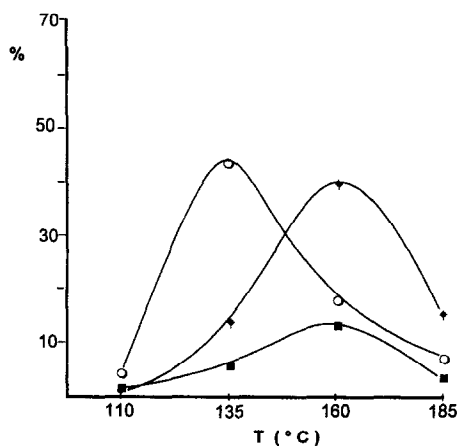
the aldehyde and the acid formation curve shows a regular decrease, while the alcohol formation increases, probably by hydrogenation of aldehydes and acids. Above 160°C all products formation decrease due probably to the deactivation of catalyst.

3.3. Effect of CO pressure

In order to study the effect of CO pressure on the carbonylation of cyclohexene, experiments

Fig. 2. Aldehyde/acid formation as a function of temperature (110 to 185°C): 120 mmol of H_2O, $Co_2(CO)_8$ 0.4 mmol, diphos 0.2 mmol, cyclohexene 9.85 mmol, P_{CO} 34 atm, THF 40 ml, reaction time 20 h, aldehyde (O), acid (■), alcohol (⊕).
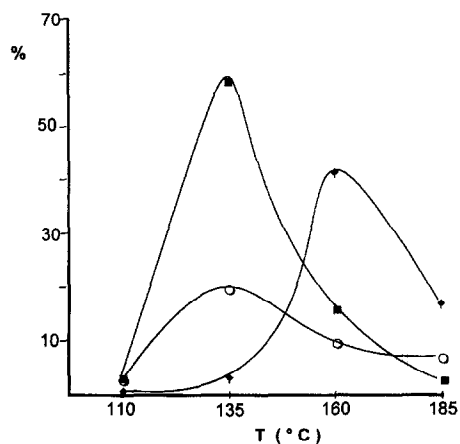
Table 1
Effect of CO pressure: reactions conditions

	% compounds/P_{CO} (atm)				
	27	34	40	47	34 [a]
Cyclohexene	16.46	25.00	15.39	16.71	4.24
Cyclohexane	14.93	13.50	12.34	9.67	11.32
Cyclohexylmethanol	5.56	13.00	5.65	5.46	3.99
Cyclochexancarbal-dehyde	41.15	44.00	29.92	27.29	20.88
Cyclohexancarboxylic acid	21.91	5.50	36.20	40.84	59.57
Total conversion	83.54	75.00	84.61	83.29	95.76
Aldehyde selectivity	49.26	58.67	35.36	32.76	62.61

Cyclohexene 9.85 mmol, $Co_2(CO)_8$ 0.4 mmol, diphos 0.2 mmol, H_2O 120 mmol, CO pressure 27–47 atm, THF 40 ml, temperature 135°C, time 20 h.
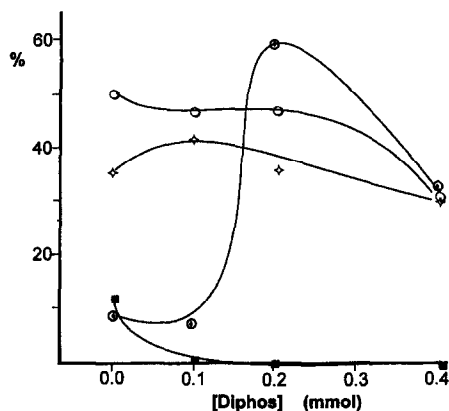[a] Experiments performed at 180 mmol of H_2O concentration.

Fig. 4. Effect of diphos concentration (0.0 to 0.4 mmol of diphos) on the cyclohexene carbonylation: 120 mmol of H_2O, $Co_2(CO)_8$ 0.4 mmol, cyclohexene 9.85 mmol, P_{CO} 34 atm, THF 40 ml, reaction time 20 h (aldehyde (○), acid (■)), 180 mmol of H_2O (aldehyde (◇), acid (◎)).

Fig. 5. Effect of $Co_2(CO)_8$ concentration (0.0 to 0.4 mmol of catalyst) on the cyclohexene carbonylation: 120 mmol of H_2O, diphos 0.2 mmol, cyclohexene 9.85 mmol, P_{CO} 34 atm, THF 40 ml, reaction time 20 h, aldehyde (○), acid (■), alcohol (⊕).

were performed with 120 mM of water and varying CO. The results reported in Table 1 show the formation of aldehyde as the main product at 34 atm of CO pressure (58.7% in selectivity). At higher CO pressure a decrease in this product is observed while the acid formation increases. This behaviour could be rationalized by a plausible stabilization of the cobalt carbonyl precursor, which favors the addition–elimination pathway (acid), over the reductive elimination (aldehyde). This was further supported by using conditions favoring the acid formation (180 mM of H_2O); when the CO pressure was 34 atm the carboxylic acid (63.0 in selectivity) was mainly formed.

3.4. Effect of $Co_2(CO)_8$ and ligand concentration

We have found that the most active catalyst was formed with a ratio $Co_2(CO)_8$/diphos = 2:1. This is shown in Fig. 4, where the highest formation of the aldehyde and acid is at 0.4 mM of $Co_2(CO)_8$ and 0.2 mM of diphos concentration. At 120 mM concentration of water the maximum concentration of aldehyde is obtained (44.0%) with a little amount of acid (Fig. 5). At 180 mM on the other hand, with the same catalyst-diphos concentration the maximum acid
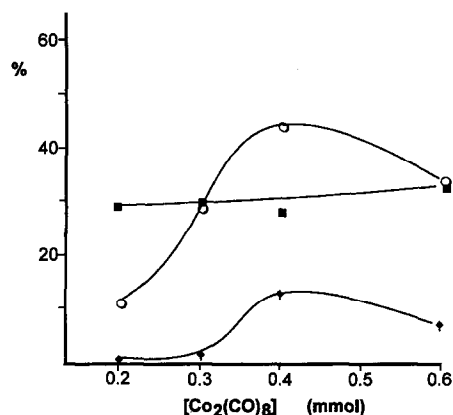
formation (59.6%) is obtained with a low yield of aldehyde (Fig. 6). These variation of aldehyde and acid yields as well as the overall selectivity of the reaction, at different water concentration, can be explained by the formation of different catalytic species.

At lower water concentration the species $Co_2(CO)_6$–diphos is plausibly responsible for aldehyde formation. Increasing the water concentration or at higher temperature or CO pressure, the Co–Co bond might be expected to break to generate $HCo(CO)_4$ known to catalyze acid formation [11]. At even higher temperature,

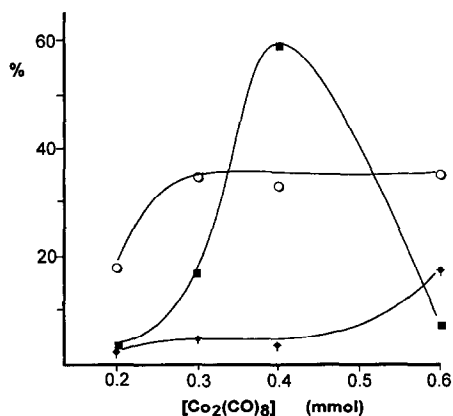Fig. 6. Effect of $Co_2(CO)_8$ concentration (0.0 to 0.4 mmol of catalyst) on the cyclohexene carbonylation: 180 mmol of H_2O, diphos 0.2 mmol, cyclohexene 9.85 mmol, P_{CO} 34 atm, THF 40 ml, reaction time 20 h, aldehyde (○), acid (■), alcohol (⊕).

the WGSR becomes more efficient increasing the H_2 concentration and thus the yield of reduced products such as alcohols or alkanes increase.

4. Conclusion

Hydroformylation and hydrocarboxylation of cyclohexene by cobalt octacarbonyl modified with diphos under water–gas shift reaction conditions are competitive reactions. But these two reactions proceed with different mechanism depending on the reaction conditions. According to the special conditions mentioned in this work, such as water concentration, temperature and the CO pressure principally, one can obtain either aldehyde or acid with different ratio of aldehyde/acid. Likewise, the alcohol formation takes place for one Reppe modification reaction [12].

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