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HYDROFORMYLATION OF PROPENE IN THE PRESENCE OF $Co_2(CO)_6[P(C_4H_9)_3]_2$

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SUMMARY

We have studied the effects of temperature and of the partial pressures of carbon monoxide and hydrogen on the isomeric distribution of hydroformylation products of propene in the presence of $Co_2(CO)_6[P(C_4H_9)_3]_2$. The marked and complex effect of the carbon monoxide pressure on the isomeric distribution of the reaction products is attributed to the progressive displacement of the phosphine by carbon monoxide in the substituted cobalt carbonyl catalytic species.

The reaction mechanism is discussed.

INTRODUCTION

A recent development in the hydroformylation of olefins has been the use of the octacarbonyldicobalt–trialkylphosphine catalytic system. A much higher percentage of the straight chain aldehyde is obtained from straight-chain olefins with this catalyst than with $Co_2(CO)_8$ alone[1,2]. Several authors have studied this new catalyst in order to throw light on the influence of the trialkylphosphine on the isomeric distribution of the aldehydes produced[1-4]. Most of the work was carried out with $Co_2(CO)_8$ and $P(C_4H_9)_3$ in the ratio $P/Co > 2$, but two experiments were carried out by Tucci[2] with P/Co ratios of 0.5 and 1, and it has been shown that the influence of the catalyst in forming straight chain aldehydes is largely independent of reaction variables such as $p(H_2)$, $p(CO)$, T, and catalyst concentration[2].

We have been interested for some time in the hydroformylation of olefins[5,6] and thus we started investigating the chemistry of trialkylphosphine-substituted cobalt carbonyls[7], and suggested a series of reactions which could explain the course of the hydroformylation in their presence. More recently we studied the behaviour of $Co_2(CO)_6[P(C_4H_9)_3]_2$ (I) under pressure of CO and H_2 at various temperatures[8]. We now describe an investigation of the influence of the reaction variables on the isomeric distribution of the aldehydes and alcohols obtained by hydroformylation of propene in the presence of $Co_2(CO)_6[P(C_4H_9)_3]_2$ (I). The preformed complex was used as catalyst so that the influence of the reaction variables could be established in the presence of a well defined compound, while propene was chosen as substrate to exclude interference from olefin isomerization.

RESULTS

(a). *Influence of CO partial pressure*

The influence of carbon monoxide partial pressure was investigated in the range 3.5–100 atm, at 150°, in two sets of experiments, one carried out at a hydrogen partial pressure of 10 atm and the other at 40 atm. The results are shown in Table 1; in Fig. 1 the percentage of n-butanal formed is plotted against the carbon monoxide partial pressure. Under a hydrogen partial pressure of 40 atm, the percentage of the straight chain isomer formed decreases initially as the carbon monoxide pressure is increased, reaches a minimum of 55% at 10 atm, increases up to 61.5% at 30 atm p(CO) and subsequently remains practically constant. The yield of aldehydes increases

TABLE 1

HYDROFORMYLATION OF PROPENE IN THE PRESENCE OF $Co_2(CO)_6[P(C_4H_9)_3]_2$ AT DIFFERENT CO PARTIAL PRESSURES

Propene 0.114 mole; toluene 30 ml; catalyst 0.200 g; temp. 150°.

p(CO) (atm)	C_3H_6 reacted (moles)	C_3H_8 (moles)	High boiling products (g)	Carbonyl cpd. (equiv.)	C_4 alcohols (moles)	n-Butanal (moles)	n-Butanol (moles)
	C_3H_6 taken (moles) (%)	C_3H_6 reacted (moles) (%)	C_4 aldehydes (g) + C_4 alcohols (g) (%)	C_3H_6 reacted (moles) (%)	C_3H_6 reacted (moles) (%)	total aldehydes (moles) (%)	total alcohols (moles) (%)
$p(H_2)$ 20 atm							
3.5	98.6	6.2	4.0	63.2	29.2	82.5	82.2
6.5	98.7	3.8	4.1	74.5	19.8	76.4	76.8
8	99.2	2.3	4.0	85.1	11.3	64.2	65.0
9	98.2	1.3	4.2	89.0	8.4	56.5	56.8
10	98.9	1.1	4.0	90.1	7.6	55.2	55.0
12.5	98.6	1.0	4.2	90.8	6.3	58.0	58.2
15	99.0	1.0	4.1	91.4	5.9	59.8	60.0
17	99.0	1.0	4.1	93.0	4.8	60.7	60.9
30	98.1	<1	4.1	95.3	2.3	61.5	61.5
60	98.6	<1	4.1	97.4	1.1	62.0	62.0
100	98.0	<1	4.1	97.6	<1	62.5	62.4
$p(H_2)$ 40 atm							
3.5	99.6	16.6	3.2	45.8	36.4	85.0	85.0
6.5	99.2	7.9	3.0	67.1	24.2	82.2	82.0
8	98.8	5.4	3.1	79.7	15.1	68.0	68.0
9	99.0	4.2	2.9	81.9	12.9	60.8	61.0
10	98.9	3.9	3.4	84.2	11.3	60.0	60.0
15	98.7	2.3	3.1	89.1	8.0	63.7	64.0
17	99.0	1.9	3.6	90.1	6.9	66.0	65.8
20	98.9	1.6	3.0	91.8	6.0	67.0	67.0
23	99.3	1.5	3.1	92.8	5.0	67.4	67.5
27	98.7	1.2	3.0	93.9	4.2	67.8	68.0
30	98.4	1.0	3.4	94.5	3.7	68.2	68.0
64	99.2	<1	2.9	97.0	1.2	68.5	68.5
90	99.0	<1	3.3	98.3	<1	69.0	69.0
133	98.9	<1	3.4	98.4	<1	70.0	70.0

with the carbon monoxide partial pressure (63% at 3.5 atm, 98% above 10 atm), while that one of C_4 alcohols decreases from 29.2% down to 1%. Olefin hydrogenation (6% at 3.5 atm CO) is reduced when the carbon monoxide partial pressure is increased.

Similar results were obtained under 40 atm of hydrogen. In all the experiments the amount of high boiling products did not exceed 3–4%; the isomeric distribution of alcohols was equal, within experimental error, to that of the aldehydes.

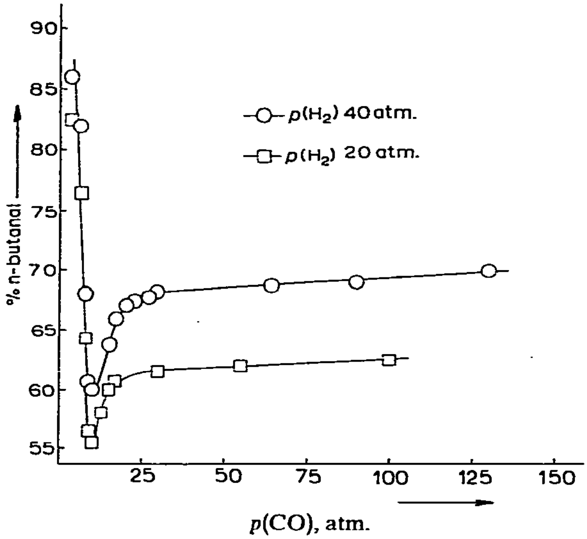

Fig. 1. Hydroformylation of propene in the presence of $Co_2(CO)_6[P(C_4H_9)_3]_2$ (temp. 150°). Influence of p(CO) on the isomeric composition of the aldehydes formed.

(*b*). *Influence of hydrogen partial pressure*

The influence of hydrogen partial pressure on the isomeric distribution of the aldehydes has been investigated in the range 10–90 atm, at 150°, under a carbon monoxide partial pressure of 30 atm. The results obtained are shown in Table 2, and

TABLE 2

HYDROFORMYLATION OF PROPENE IN THE PRESENCE OF $Co_2(CO_6[P(C_4H_9)_3]_2$ AT VARIOUS H_2 PARTIAL PRESSURES

Propene 0.114 mole; toluene 30 ml; catalyst 0.200 g; p(CO) 30 atm; temp. 150°.

$p(H_2)$ (atm)	C_3H_6 reacted (moles)	C_3H_8 (moles)	High boiling products (g)	Carbonyl cpd. (equiv.)	C_4 alcohols (moles)	n-Butanal (moles)	n-Butanol (moles)
	C_3H_6 taken (moles) (%)	C_3H_6 reacted (moles) (%)	C_4 aldehydes (g)+ C_4 alcohols (g) (%)	C_3H_6 reacted (moles) (%)	C_3H_6 reacted (moles) (%)	total aldehydes (moles) (%)	total alcohols (moles) (%)
10	99.1	<1	5.9	96.8	1.0	58.0	58.0
20	99.3	<1	4.1	96.3	2.3	61.5	61.5
30	98.3	<1	4.0	95.2	2.9	65.0	65.0
40	98.7	1.0	3.4	94.3	3.7	68.2	68.0
65	99.3	1.0	3.0	91.8	6.1	68.4	68.5
90	99.4	1.3	2.4	89.1	8.5	68.6	68.5

in Fig. 2 the percentage of n-butanal formed is plotted against $p(H_2)$. When the hydrogen partial pressure is increased from 10 atm to 40 atm the percentage of n-butanal increases rapidly from 58% to 68% and then remains practically constant; the yield of aldehydes decreases from 96.8 to 89.1% while that of alcohols increases from 1 to 8.5%.

At a carbon monoxide partial pressure of 4 atm the results are independent of the hydrogen partial pressure (Fig. 2).

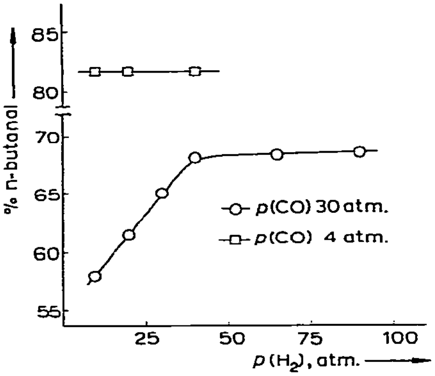

Fig. 2. Hydroformylation of propene in the presence of $Co_2(CO)_6[P(C_4H_9)_3]_2$. Influence of $p(H_2)$ on the isomeric composition of the aldehydes formed.

(c). *Influence of temperature*

Temperatures of 130–180° were used, with a hydrogen partial pressure of 40 atm and a carbon monoxide partial pressure of 30 atm. The results, shown in Table 3, show that the percentage of n-butanal decreases from 70.5 to 66% when the temperature is increased from 130 to 180°; at the same time the yield of aldehydes decreases from 94 to 76% while that of alcohols increases from 1 to 19%.

TABLE 3

HYDROFORMYLATION OF PROPENE IN THE PRESENCE OF $Co_2(CO)_6[P(C_4H_9)_3]_2$ AT VARIOUS TEMPERATURES

Propene 0.114 mole; toluene 30 ml; catalyst 0.200 g; $p(CO)$ 30 atm; $p(H_2)$ 40 atm.

Temp. (°C)	C_3H_6 reacted (moles)	C_3H_8 (moles)	High boiling products (g)	Carbonyl cpd. (equiv.)	C_4 alcohols (moles)	n-Butanal (moles)	n-Butanol (moles)
	C_3H_6 taken (moles) (%)	C_3H_6 reacted (moles) (%)	C_4 aldehydes (g) + C_4 alcohols (g) (%)	C_3H_6 reacted (moles) (%)	C_3H_6 reacted (moles) (%)	total aldehydes (moles) (%)	total alcohols (moles) (%)
130	98.5	<1	2.7	95.0	1.3	70.5	70.0
150	98.6	1.0	2.4	94.5	3.7	68.2	68.0
170	99.0	1.7	3.5	89.2	8.5	66.5	66.5
180	99.2	4.0	2.9	80.0	15.5	66.1	66.0

DISCUSSION

The results reported above show a definite influence of reaction conditions on the course of the hydroformylation of propene catalysed by $Co_2(CO)_6[P(C_4H_9)_3]_2$. The carbon monoxide partial pressure has a greater influence than the other variables tested on the reaction product composition. From Figs. 1 and 3 clearly appears that change in the carbon monoxide partial pressure, in the 3.5–10 atm pressure range, affects the isomeric distribution of the aldehydes obtained by hydroformylation of propene in one direction in presence of (I) and in the other in presence of $Co_2(CO)_8$[5]. At higher carbon monoxide partial pressures the influence is in the same direction with both catalysts: initially there is a rapid increase of the percentage of the straight chain isomer, but at pressures higher than 30 atm this remains practically constant.

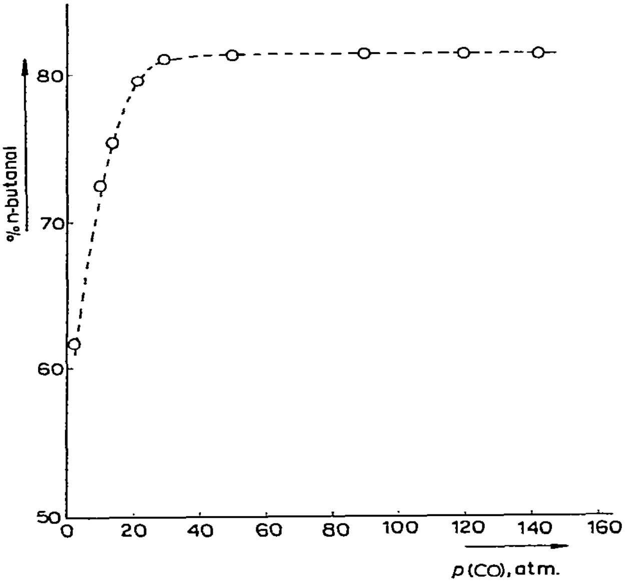

Fig. 3. Hydroformylation of propene in the presence of $Co_2(CO)_8$ ($p(H_2)$ 80 atm.; temp. 110°). Influence of $p(CO)$ on the isomeric composition of the aldehydes formed.

The influence of the carbon monoxide partial pressure on the isomeric distribution of the aldehydes formed in the hydroformylation of olefins in the presence of $Co_2(CO)_8$ has been tentatively attributed[5,6] to the influence of carbon monoxide on the concentration of two catalytically active cobalt carbonyl hydrides which, for steric reasons, determine the ratios of the isomeric aldehydes formed. Recently we suggested a mechanism of the hydroformylation of olefins in the presence of (I)[7] in which the hydride $HCo(CO)_3P(C_4H_9)_3$ is a catalytic intermediate which reacts with the olefine to give the corresponding alkyl derivative. It seems that the presence of the bulky tributylphosphine molecule coordinated to the cobalt is responsible, probably for steric reasons, for the higher selectivity of this catalyst compared with that of $HCo(CO)_4$.

The decrease of the percentage of n-butanal formed in the hydroformylation of propene in the presence of (I) when the carbon monoxide partial pressure is increased from 3.5 to 10 atm can be attributed to the progressive displacement of the phosphine in the complex by carbon monoxide. Consistent with this, the influence of the carbon monoxide partial pressure on the isomeric distribution of the hydroformylation products of propene in the presence of (I) at pressures higher than 10 atm is similar to that observed in the presence of $Co_2(CO)_8$.

Carbon monoxide at atmospheric pressure and room temperature in the presence of light displaces the phosphine from (I) according to eqn. (1)[8,9].

$$Co_2(CO)_6[P(C_4H_9)_3]_2+CO \rightleftarrows Co_2(CO)_7P(C_4H_9)_3+P(C_4H_9)_3 \qquad (1)$$

In the absence of light this reaction is rather slow, but conversions are observed under hydroformylation conditions[8]. Furthermore, in the presence of hydrogen appreciable displacement of the phosphine from (I) can occur even at low pressures of carbon monoxide.

The proposed mechanism receives support from the observation that when the hydroformylation with (I) as catalyst is carried out in the presence of an excess of $P(C_4H_9)_3$ (Table 4), the carbon monoxide partial pressure has no influence on the isomeric distribution of the reaction products; under these conditions unsubstituted cobalt carbonyls are absent according to IR measurements.

TABLE 4

HYDROFORMYLATION OF PROPENE IN THE PRESENCE OF $Co_2(CO)_6[P(C_4H_9)_3]_2$ AND $P(C_4H_9)_3$ AT VARIOUS CO PARTIAL PRESSURES

Propene 0.114 mole; toluene 30 ml; catalyst 0.200 g; $P(C_4H_9)_3$ 1.6 g; $p(H_2)$ 40 atm; temp. 150°.

p(CO) (atm)	C_3H_6 reacted (moles) C_3H_6 taken (moles) (%)	C_3H_8 (moles) C_3H_6 reacted (moles) (%)	High boiling products (g) C_4 aldehydes (g) + C_4 alcohols (g) (%)	Carbonyl cpd. (equiv.) C_3H_6 reacted (moles) (%)	C_4 alcohols (moles) C_3H_6 reacted (moles) (%)	n-Butanal (moles) total aldehydes (moles) (%)	n-Butanol (moles) total alcohols (moles) (%)
5	98.7	12.5	4.0	52.5	34.3	89.0	89.0
9	99.0	6.4	4.2	71.2	21.4	89.0	90.0
13	99.1	4.3	4.3	81.4	13.1	89.0	89.0
15	98.2	3.5	4.6	84.0	11.7	89.0	89.5
60	98.7	1.1	4.7	96.0	2.1	89.0	88.5
130	99.2	<1	4.3	98.0	<1	89.0	89.0

The influence of the hydrogen partial pressure and of temperature on the isomeric distribution of the aldehydes obtained by hydroformylation of propene in the presence of (I) under a carbon monoxide partial pressure of 30 atm is analogous to that observed in the presence of $Co_2(CO)_8$. This is as expected, since at this carbon monoxide partial pressure a considerable percentage of the tributylphosphine substituted cobalt carbonyls is converted into the catalytically more active unsubstituted derivatives[8].

The results reported in Fig. 2 for hydroformylation experiments carried out at a carbon monoxide partial pressure of 4 atm and hydrogen pressures in the range 10–40 atm clearly prove that when the phosphine displacement in the catalyst is negligible the influence of the hydrogen partial pressure on the isomeric distribution of the products is also negligible.

Although the problem has long been discussed it is not yet clear which stage of the reaction is responsible for the high selectivity of addition of the formyl group to the terminal position of the olefin by hydroformylation in the presence of (I). Much attention has been given to double bond isomerization in the olefin[2-4], it has been shown that such isomerization during hydroformylation of olefins is diminished by the presence of phosphines and this fact has been related to the higher percentage of the straight chain isomer obtained by hydroformylation of α-olefins in the presence of (I) than in the presence of $Co_2(CO)_8$. However, we have previously demonstrated that olefin isomerization is very small during the hydroformylation, even with $Co_2(CO)_8$ as catalyst, under high carbon monoxide partial pressure, and thus the isomeric distribution of products is not influenced by olefin isomerization. Thus even if the presence of a phosphine does inhibit the isomerization of olefins it is unlikely that this affects the product isomer distribution. Furthermore, we have recently shown, by studying the hydroformylation of (+)-(*S*)-3-methyl-1-hexene[10], that a formyl group may be introduced on a methyl group of the olefin by direct formylation without isomerization, and thus occurrence of olefin isomerization before hydroformylation is not necessary to explain the formation of products.

When the hydroformylation of olefins is carried out with a $Co_2(CO)_8$–$P(C_4H_9)_3$ catalytic system with a P/Co ratio greater than 1, it appears that the reaction is catalyzed by tributyl substituted cobalt carbonyls. When the P/Co ratio is equal or lower than 1 and the carbon monoxide partial pressure is higher than 10 atm then the reaction is catalyzed by both unsubstituted and substituted cobalt carbonyls.

EXPERIMENTAL

Materials

Propene, prepared by dehydration of isopropyl alcohol on activated alumina, dried on P_2O_5, was 99% pure.

Tributylphosphine (Fluka A.G.) 99% pure was used after distillation. Hexacarbonylbis(tributylphosphine)dicobalt was prepared as described previously[7].

Quantitative determination of aldehydes

This was carried out by reacting the sample with hydroxylamine hydrochloride and titrating the hydrochloric acid liberated.

Distribution of isomeric aldehydes and alcohols

All determinations were carried out by GLC using a Perkin–Elmer vapour fractometer Mod. F 11.

The hydroformylation products of propene were directly analyzed on a column packed with polypropylenglycol monostearate on chromosorb.

Apparatus for hydroformylation reactions

All experiments were carried out in the high pressure equipment described in a previous paper[5].

Hydroformylation of propene

Hydroformylation of propene was carried out as previously described[5] using $Co_2(CO)_6[P(C_4H_9)_3]_2$ as catalyst.

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