

Journal of Organometallic Chemistry, 417 (1991) 65–76
Elsevier Sequoia S.A., Lausanne
JOM 21861

Activation of molecular hydrogen in cobalt-catalyzed hydroformylation *

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(Received January 10th, 1991)

Abstract

The mechanism of the activation of molecular hydrogen in cobalt-catalyzed hydroformylation of olefins has been studied by high pressure IR spectroscopy using $\text{HCo}(\text{CO})_4$ (**1**) under 100 bar H_2 (or D_2) in the absence or presence of CO at room temperature. The treatment of **1** with 100 bar H_2 resulted in the formation of $\text{Co}_2(\text{CO})_8$ (**2**) and a small amount of $\text{Co}_4(\text{CO})_{12}$ (**3**), and the transient formation of $\text{HCo}_3(\text{CO})_9$ (**4**). In the reaction of **1** with one equivalent of 3,3-dimethyl-butene-1 under 100 bar H_2 both hydrogenation and hydroformylation occur, but the former is much faster. In the presence of large amounts of **1** the predominant path for the hydrogenation of the olefin involves the reaction of two equivalents of **1** with the olefin even under 100 bar of H_2 . Under a very low partial pressure of CO the stability of **1** is increased and the hydrogenation significantly slowed down. The preferred path of the hydroformylation of the olefin involves the addition of H_2 and CO from gas phase even in the presence of large amount of $\text{HCo}(\text{CO})_4$ (**1**) under 100 bar H_2 and 2.3 bar CO at room temperature. The studies reveal that the mechanism of H_2 activation in the presence of $\text{HCo}(\text{CO})_4$ (**1**) is highly dependent on the reaction conditions. Under 100 bar H_2 and at room temperature the activation of molecular hydrogen starts at a coordinatively unsaturated acyl cobalt carbonyl, yielding an aldehyde and an unknown cobalt species. It is believed that this species is a coordinatively unsaturated hydrido cobalt carbonyl like $\{\text{HCo}(\text{CO})_3\}$, and can activate and catalytically hydroformylate the olefin.

Preface

The late Piero Pino was fascinated with the mechanistic aspects of homogeneous catalysis and always challenged himself as well as his colleagues and students with

* This paper is dedicated to the memory of Professor Piero Pino, who deceased on July 9th, 1989.

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To gain further information on the mechanism of hydrogen activation in the cobalt-catalyzed hydroformylation we have investigated the reaction of $\text{HCo}(\text{CO})_4$ (**1**) with olefins in the presence of hydrogen or deuterium. The experiments were aimed at distinguishing between stoichiometric and catalytic reactions involving the activation of H_2 or D_2 by various cobalt species. Some preliminary results for the reaction of **1** with cyclopentene under H_2 were published recently [9].

Results and discussion

Since two well-established equilibria (eq. 7 [10] and eq. 8 [11])



must be taken into account in a cobalt catalyst system under CO/H_2 , we determined the extent to which such processes occur under the conditions used in this study. We investigated the transformation of $\text{HCo}(\text{CO})_4$ (**1**) to $\text{Co}_2(\text{CO})_8$ (**2**) and H_2 starting from **1** under 100 bar H_2 at 25°C in n-hexane (Table 1, Fig. 1). The reaction occurs slowly, and after 50 h the relative concentration of **1** and **2** were still far from the equilibrium value [10]. The formation of a small amount of $\text{Co}_4(\text{CO})_{12}$ (**3**) and $\text{HCo}_3(\text{CO})_9$ (**4**) [12] was also detected. While the concentration of **3** steadily increased, that of **4** reached a maximum value after 2 h, then slowly disappeared. The formation of **4** is in accord with the previously observed equilibrium (eq. 9) [12],

Table 1

Transformation of $\text{HCo}(\text{CO})_4$ (**1**) (23 mmol/l) to $\text{Co}_2(\text{CO})_8$ (**2**) and H_2 starting from **1** under 100 bar H_2 at 25°C in n-hexane

Time (h)	$\text{HCo}(\text{CO})_4$ (mmol/l)	$\text{Co}_2(\text{CO})_8$ (mmol/l)	$\text{Co}_4(\text{CO})_{12}$ (mmol/l)	$\Sigma\text{Co}(\text{CO})_x^a$ (mmol/l)
0	23.00	nd	nd	23.00
0.5	22.56	0.17	0.01	23.10
1.0	22.16	0.48	0.03	23.23
2.0	21.42	0.87	0.04	23.32
3.5	19.99	1.42	0.07	23.12
5.0	18.85	1.93	0.08	23.05
7.0	17.93	2.44	0.13	23.31
9.0	16.85	2.88	0.15	23.21
12.0	15.71	3.36	0.18	23.14
17.5	14.28	4.06	0.21	23.25
21.5	13.71	4.21	0.24	23.07
25.0	12.85	4.53	0.27	22.99
36.0	12.39	4.52	0.28	22.55
50.0	12.25	4.67	0.39	23.14

^a $\Sigma\text{Co}(\text{CO})_x = \text{HCo}(\text{CO})_4 + 2 \text{Co}_2(\text{CO})_8 + 4 \text{Co}_4(\text{CO})_{12}$.

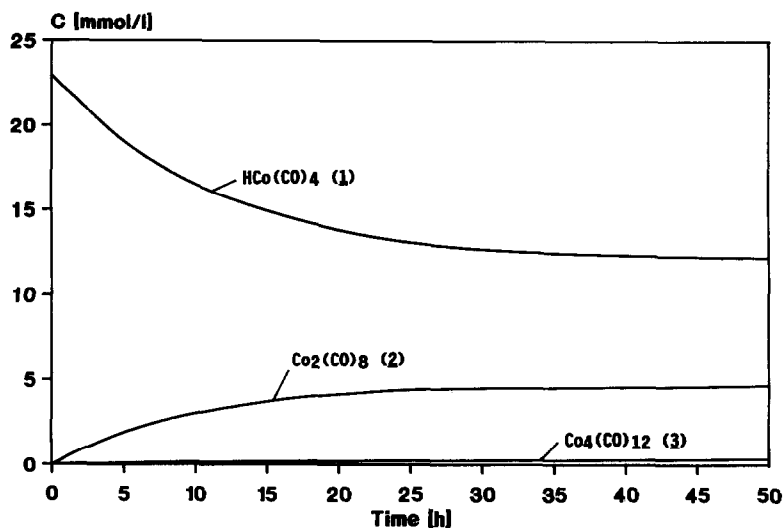
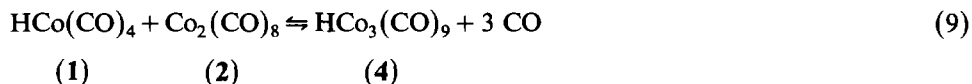


Fig. 1. Transformation of $\text{HCo}(\text{CO})_4$ (1) to $\text{Co}_2(\text{CO})_8$ (2) and H_2 starting from 1 under 100 bar H_2 at 25°C in n-hexane.

and its disappearance is due to the formation of a small amount of CO by decarbonylation of 2.



The reaction of $\text{HCo}(\text{CO})_4$ (1) with one equivalent of olefin was studied under 100 bar H_2 in n-hexane at 25°C . We used 3,3-dimethyl-1-butene as substrate since it gives only one aldehyde upon hydroformylation. The disappearance of $\text{HCo}(\text{CO})_4$ (1) and the formation of $\text{Co}_2(\text{CO})_8$ (2) were at least twice as fast in the presence than in the absence of the olefin (Table 2, Fig. 2). After 15 h the concentration of 2

Table 2

Reaction of $\text{HCo}(\text{CO})_4$ (1) (22.21 mmol/l) with 3,3-dimethyl-1-butene (22.3 mmol/l) under 100 atm H_2 at 25°C in n-hexane

Time (h)	$\text{HCo}(\text{CO})_4$ (mmol/l)	$\text{Co}_2(\text{CO})_8$ (mmol/l)	$\text{Co}_4(\text{CO})_{12}$ (mmol/l)	$\Sigma\text{Co}(\text{CO})_x^a$ (mmol/l)	Aldehyde (mmol/l)
0.1	21.59	0.23	0.02	22.14	nd
0.4	20.50	0.73	0.11	22.38	nd
1.1	17.63	1.84	0.23	22.21	nd
2.0	14.55	2.97	0.37	21.95	0.52
4.0	10.74	4.51	0.59	22.13	1.14
6.0	8.6	5.12	0.78	22.08	1.38
12.0	5.62	6.01	1.10	22.03	1.88
18.5	4.68	5.80	1.31	21.54	2.06
31.5	4.44	5.37	1.53	21.29	2.69
49.1	4.49	4.38	1.84	20.59	3.13

^a $\Sigma\text{Co}(\text{CO})_x = \text{HCo}(\text{CO})_4 + 2 \text{Co}_2(\text{CO})_8 + 4 \text{Co}_4(\text{CO})_{12}$.

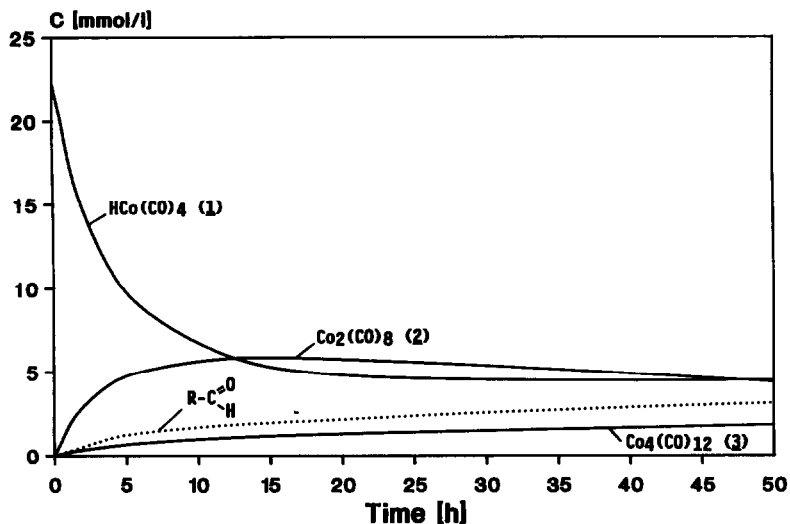


Fig. 2. Reaction of $\text{HCo}(\text{CO})_4$ (1) (22.2 mmol/l) with 3,3-dimethyl-1-butene (22.3 mmol/l) under 100 atm H_2 at 25°C in *n*-hexane.

reached a maximum value that was considerably higher than that predicted by equilibrium (7) [10]. This indicated that 1 reacted with 3,3-dimethyl-1-butene, and that the reaction was accompanied by the formation of 2. It was noticed that the amount of the olefin used up was larger than that of the aldehyde produced. This suggested that under these conditions, the olefin was partly hydrogenated by $\text{HCo}(\text{CO})_4$ (1) and/or hydrogen. Since we used *n*-hexane as solvent, GLC separation of the hydrogenation product (3,3-dimethylbutane) from the solvent was difficult and so, we repeated the reaction of $\text{HCo}(\text{CO})_4$ (1) with 3,3-dimethyl-1-butene in iso-octane under 100 bar H_2 at 25°C . The outcome of the reaction in iso-octane was practically as that in *n*-hexane. The major product was $\text{Co}_2(\text{CO})_8$ (2) and only a slow formation of $\text{Co}_4(\text{CO})_{12}$ (3) was noticed. After 42 h 30% of the olefin was hydrogenated to 3,3-dimethylbutane and 10% hydroformylated to 4,4-dimethylpentanal. Although these results confirmed that significant amounts of the olefin were hydrogenated, we could not make a distinction between stoichiometric hydrogenation involving two equivalents of 1 and catalytic hydrogenation using H_2 from the gas phase.

One could distinguish between stoichiometric and catalytic hydrogenation by labeling experiments using $\text{HCo}(\text{CO})_4$ (1) and D_2 provided the H/D exchange between 1 and D_2 is much slower than the hydrogenation. While the H/D exchange occurs at an easily measurable rate at 80°C under 40 bar CO and 40 bar D_2 [13], only very slow H/D exchange was observed at 25°C with 1 under 100 bar D_2 (Table 3). Since the H/D exchange between 1 and D_2 is sufficiently slow at 25°C we investigated the reaction of equimolar amounts of $\text{HCo}(\text{CO})_4$ (1) and cyclopentene under 100 bar D_2 at 25°C in *n*-heptane (Table 4). The rates of the disappearance of 1 as well as the formation of 2 are much faster in the presence than in the absence of the olefin (Fig. 3). The amount of 2 formed was again greater than that predicted by equilibrium (7) [10], and the hydrogenation was faster than the hydroformylation of the olefin. IR and GLC-MS analysis of the isotopic composi-

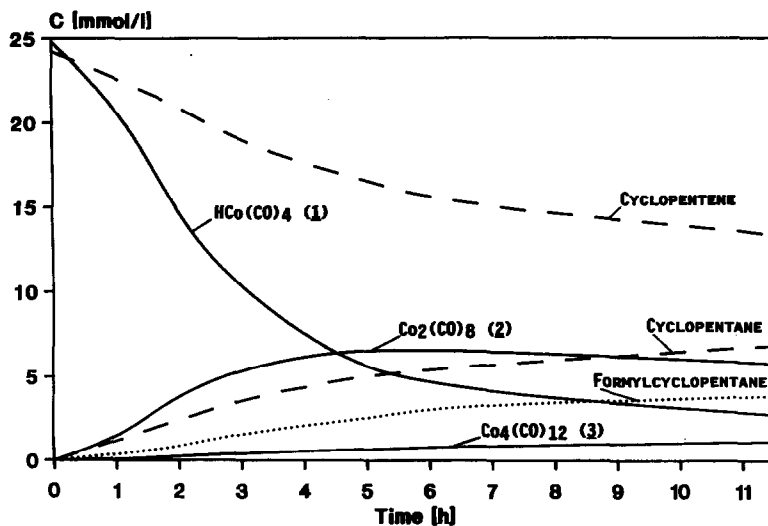


Fig. 3. Reaction of $\text{HCo}(\text{CO})_4$ (1) (24.77 mmol/l) with cyclopentene (24.2 mmol/l) under 100 atm D_2 at 25°C in n-heptane (sum of H- and D-containing products shown).

pressure of CO (0.6–2.2 bar) to suppress the hydrogenation of olefin. With octene-1 as the olefin, present in an excess with respect to 1 and 0.65 bar CO, there was a rapid decrease in the concentration of $\text{HCo}(\text{CO})_4$ (1) accompanied by a rapid increase in that of $\text{Co}_2(\text{CO})_8$ (2) and a slow increase in the concentration of aldehyde (Table 5, Fig. 5). Fast formation of acyl cobalt tetracarbonyl,

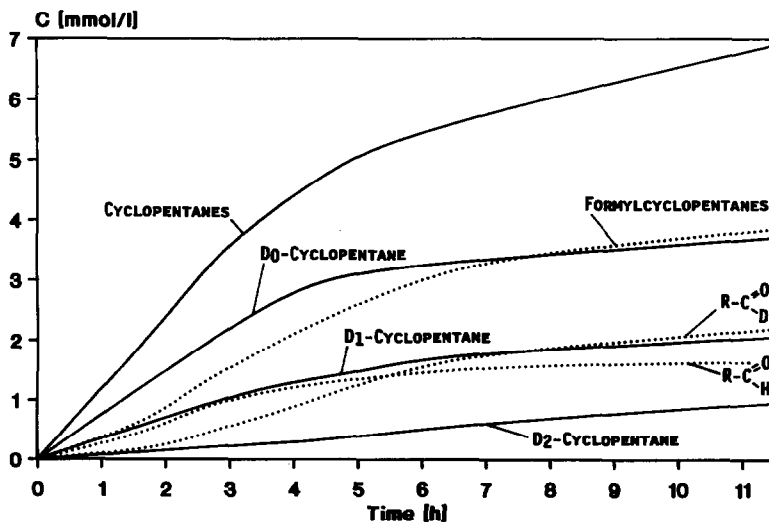


Fig. 4. Formation of deuterated and nondeuterated products in the reaction of $\text{HCo}(\text{CO})_4$ (1) (24.77 mmol/l) with cyclopentene (24.2 mmol/l) under 100 atm D_2 at 25°C in n-heptane.

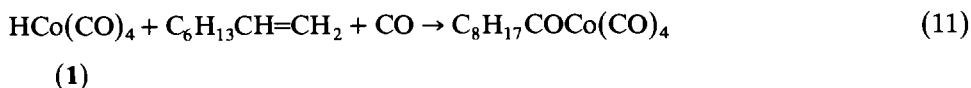
Table 5

Reaction of $\text{HCo}(\text{CO})_4$ (1) (13.35 mmol/l) with octene-1 (463 mmol/l) under 0.65 bar CO and 100 atm H_2 at 25 °C in n-hexane

Time (h)	$\text{HCo}(\text{CO})_4$ (mmol/l)	$\text{Co}_2(\text{CO})_8$ (mmol/l)	$[\text{Co}(\text{CO})_x]_t$ ^a (mmol/l)	$A(2103)$ ^b	Aldehyde (mmol/l)
0	13.35	0			
0.03	4.92	2.46	3.51	0.073	
0.13	3.42	2.60	4.73	0.122	
0.25	2.54	2.93	4.95	0.161	
0.45	0.35	3.85	5.30	0.218	2.29
0.80	nd ^c	4.08	5.19	0.202	4.59
1.65	nd	4.20	4.95	0.135	11.64
2.55	nd	4.15	5.05	0.087	15.09
3.78	nd	4.98	3.39	0.046	19.22
4.90	nd	4.43	4.49	0.020	20.54

^a $[\text{Co}(\text{CO})_x]_t = [\text{HCo}(\text{CO})_4]_{t=0} - \{[\text{HCo}(\text{CO})_4]_t + 2[\text{Co}_2(\text{CO})_8]_t\}$. ^b $A(2103)$: absorbance value for $\text{RCOCo}(\text{CO})_4$ at 2103 cm^{-1} ($d_{\text{cell}} = 0.059 \text{ cm}$). ^c nd = not determined.

$\text{C}_8\text{H}_{17}\text{COC}(\text{CO})_4$ was also observed (eq. 11), as shown by the rapidly increasing intensity of the band at 2103 cm^{-1} assigned to this species [15].



The formation of the aldehyde continued even after 1 had disappeared and the concentration of 2 has reached a constant level. The aldehyde must have been formed by either the reaction of $\text{C}_8\text{H}_{17}\text{COC}(\text{CO})_4$ and H_2 , or by catalytic hydroformylation of the olefin by the carbon monoxide and hydrogen present in the

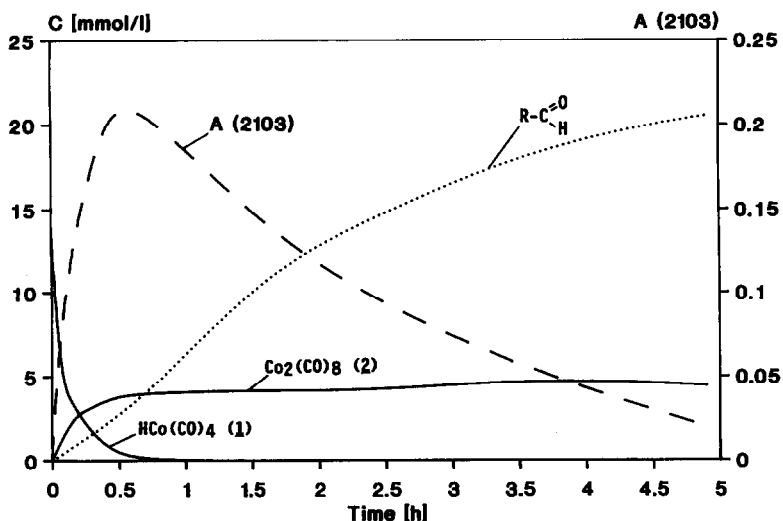


Fig. 5. Reaction of $\text{HCo}(\text{CO})_4$ (1) (13.35 mmol/l) with octene-1 (463 mmol/l) under 0.65 bar CO and 100 atm H_2 at 25 °C in n-hexane.

gas phase. After 5 h the molar ratio aldehyde/ $\text{HCo}(\text{CO})_4$ was 1.77. This experiment shows that both hydrogen and carbon monoxide can be activated by a soluble cobalt complex at 25 °C. Even under this low pressure (0.65 bar) gaseous carbon monoxide is the source of the aldehyde carbonyl, and no decarbonylation of $\text{Co}_2(\text{CO})_8$ (**2**) to $\text{Co}_4(\text{CO})_{12}$ (**3**) takes place. Furthermore, there seems to be no relationship between the changes in the concentrations of **1** and/or **2** and the increase in the concentration of the aldehyde.

In view of the continuing discussions about the possible role of $\text{HCo}(\text{CO})_4$ (**1**) in catalytic hydroformylation, it was of interest to ascertain whether the preferred route to the aldehyde in the presence of a large concentration of **1** still involves activation of H_2 . A further experiment was carried out with **1** in the liquid phase and 100 bar D_2 and 2.3 bar CO in the gas phase. It should be noted here that under these conditions the reaction of $\text{Co}_2(\text{CO})_8$ (**2**) with H_2 is extremely slow; after 48 h, the $\text{HCo}(\text{CO})_4$ (**1**) in the solution can only be detected by its characteristic odor. It appears that aldehydes containing deuterioformyl groups, indicating the activation of gaseous D_2 , are formed even in the first hours when a very large concentration of **1** is still present in solution. As expected, protioformyl groups are formed when the concentration of **1** is high, and are practically not formed at all in the absence of **1** (Table 6, Fig. 6). This experiment shows that under the conditions used, formation of aldehydes from gaseous D_2 activated by a catalytic species present in very small concentration, is faster than the formation of aldehydes arising directly from $\text{HCo}(\text{CO})_4$ (**1**). After reduction of the aldehydes, mass spectral analysis of the alcohols showed that the largest part of the aldehydes (47%) contained two deuterium atoms. Thus, the catalytic species which is able to activate D_2 is also able to add the first deuterium atom to the olefinic double bond. Only 5% of the aldehydes contains no deuterium, and these must arise from the reactions of two molecules of $\text{HCo}(\text{CO})_4$ (**1**) with the olefin. Analysis of the d_1 -aldehyde showed 56% of it to contain a CDO group thus confirming that the catalytic complex activating CO and D_2 can react with the olefin.

Table 6

Reaction of $\text{HCo}(\text{CO})_4$ (**1**) (48.74 mmol/l) with 3,3-dimethyl-1-butene (1.61 mol/l) under 2.3 bar CO and 100 atm D_2 at 25 °C in n-hexane

Time (h)	$\text{HCo}(\text{CO})_4$ (mmol/l)	$\text{Co}_2(\text{CO})_8$ (mmol/l)	$[\text{Co}(\text{CO})_x]_t$ ^a (mmol/l)	$A(2103)$ ^b	RCHO (mmol/l)	RCDO (mmol/l)
0	48.74	0	0	0	0	0
2.0	35.44	3.73	5.84	0.115	2.39	3.24
2.5	33.03	4.39	6.93	0.135	2.88	3.70
3.0	30.82	5.15	7.62	0.155	3.23	4.34
3.83	28.09	6.77	7.11	0.170	4.32	6.27
4.83	23.16	7.96	9.66	0.180	5.87	7.33
6.0	17.98	nd ^c	–	0.212	6.77	9.85
7.0	14.79	nd	–	0.240	9.22	12.46
8.5	10.63	nd	–	0.255	10.66	16.23
10.0	7.40	nd	–	0.260	11.71	19.04
12.0	3.65	nd	–	0.265	12.48	25.07
21.5	0	nd	–	0.170	14.25	40.12

^a $[\text{Co}(\text{CO})_x]_t = [\text{HCo}(\text{CO})_4]_{t=0} - \{[\text{HCo}(\text{CO})_4]_t + 2[\text{Co}_2(\text{CO})_8]_t\}$. ^b $A(2103)$: absorbance value for $\text{RCOC}(\text{CO})_4$ at 2103 cm^{-1} ($d_{\text{cell}} = 0.059 \text{ cm}$). ^c nd = not determined.

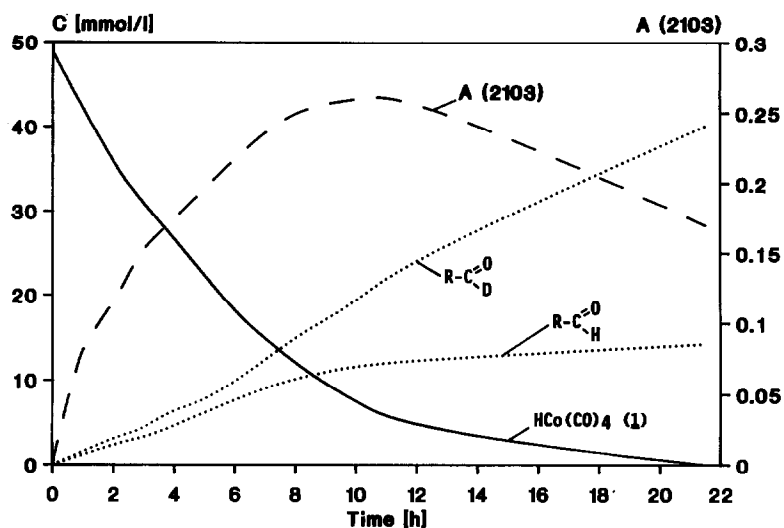
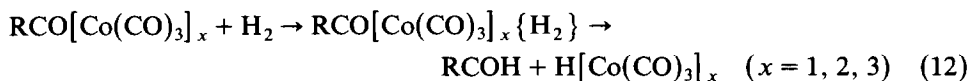


Fig. 6. Reaction of $\text{HCo}(\text{CO})_4$ (1) (48.74 mmol/l) with 3,3-dimethyl-1-butene (1.61 mol/l) under 2.3 bar CO and 100 atm D_2 at 25°C in *n*-hexane.

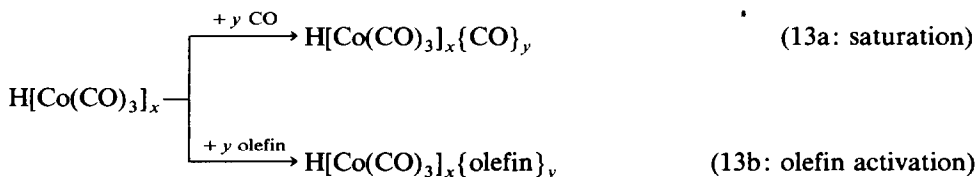
At the low carbon monoxide pressures used in these experiments a reaction of $\text{Co}_2(\text{CO})_8$ (2) with a Lewis base [16] (e.g. the formed aldehydes) could also be involved in the activation of H_2 . However, no spectroscopic evidence was found for the formation of $\text{HCo}(\text{CO})_4$ (1) when 2 (14 mmol/l) and 1-nonanal (43 mmol/l) were stirred together under 2.4 bar CO and 100 bar H_2 for 48 h in *n*-hexane.

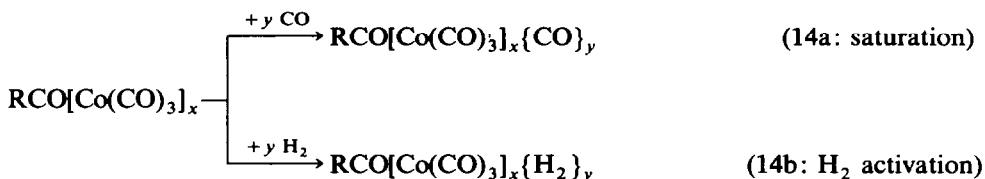
Conclusions

These studies show that the activation of molecular hydrogen in the presence of $\text{HCo}(\text{CO})_4$ (1) and 100 bar H_2 at room temperature starts at a coordinatively unsaturated acyl cobalt carbonyl, yielding an aldehyde and an unknown cobalt species (eq. 12). This species, in turn, is able to activate and catalytically hydroformylate the olefin. It is likely that this species is a coordinatively unsaturated complex containing one or more cobalt atoms ($x = 1$: $\text{HCo}(\text{CO})_3$, $x = 3$: $\text{HCo}_3(\text{CO})_9$).

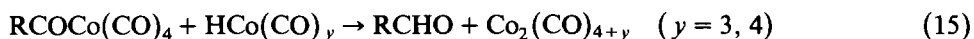


Further evidence was found that the partial pressure of carbon monoxide has a profound effect in the hydroformylation. The role of CO may be connected with two steps of the catalytic cycle under our conditions, by saturation of the coordinatively unsaturated species which activate the olefin (eq. 13a,b) or the molecular hydrogen (eq. 14a,b), respectively.

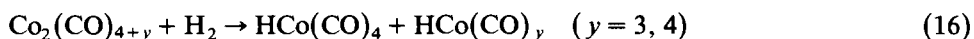




This could mean that the decrease of the concentration of $\text{RCO[Co(CO)}_3\text{]}_x$ is more sensitive to the higher partial pressure of CO than that of $\text{H[Co(CO)}_3\text{]}_x$. This could result in slower H_2 activation and subsequently slower catalytic hydroformylation. Furthermore, when $x = 1$ and the HCo(CO)_4 (1) concentration is high, the aldehyde can also be formed by reaction of the saturated RCOCO(CO)_4 and HCo(CO)_4 (1) or $\{\text{HCo(CO)}_3\}$ (eq. 15).



The reaction of the formed $\text{Co}_2(\text{CO})_{4+y}$ with hydrogen (eq. 16) does not seem to be the preferred path for hydrogen activation under our conditions.



At higher temperatures and partial pressure of CO, however, reaction (16) probably is involved in the catalytic hydroformylation of olefins, as was suggested recently [17].

Experimental

All operations were performed under N_2 , H_2 or D_2 . The solvents (products of Fluka AG) were purified and dried by the usual methods. 3,3-Dimethyl-1-butene and octene-1 were purchased from Fluka AG and distilled over Na under N_2 immediately before use. Deuterium (99% isotopic purity) was purchased from L'Air Liquide Belge. High pressure experiments were performed in a 1000 ml stainless steel autoclave equipped with magnetic stirring and jacketed cooling. Samples were withdrawn under pressure directly into a thermostated high-pressure IR cell. A pressure cell of the type published by Noack [18], equipped with a heating/cooling mantle (connected to a thermostat), modified in some minor details, was used for IR spectral measurements [19]. IR spectra were recorded on a Perkin-Elmer Model 983 spectrometer combined with a Perkin-Elmer Data Station 3600.

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