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THE CATALYTIC ACTIVITY OF METAL CARBONYL CLUSTER COMPOUNDS. HYDROFORMYLATION AND HYDROESTERIFICATION CATALYZED BY $Co_4(CO)_{12}$ AND $Co_2(CO)_8$

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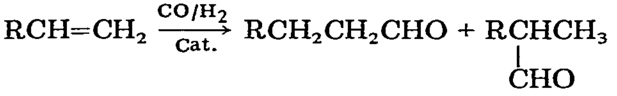
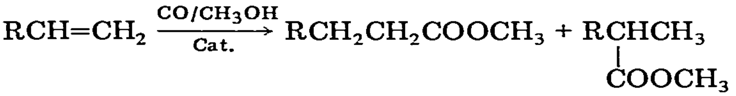
Summary

The carbonyl complexes $Co_2(CO)_8$ and $Co_4(CO)_{12}$ catalyze the hydroformylation and hydroesterification reactions via the same catalytic cycle. The entry into this cycle via $HCo(CO)_3$ is easier with $Co_4(CO)_{12}$ than with $Co_2(CO)_8$, and so the former is the more active catalyst.

Since the discovery of the hydroformylation [1] and the hydrocarboxylation reaction [2], the catalytic activity of dicobalt octacarbonyl $Co_2(CO)_8$ has been much studied [3]. Tetracobalt dodecacarbonyl $Co_4(CO)_{12}$ is known to catalyze the hydroformylation reaction [4], but no detailed investigation has been described, probably because it was assumed that the complex would be converted into $Co_2(CO)_8$ under the reaction conditions [5]. In the light of recent results by Bor et al. [6], who found that the conversion of $Co_4(CO)_{12}$ into $Co_2(CO)_8$ is rather slow even at high pressures of carbon monoxide, we reinvestigated the catalysis by $Co_2(CO)_8$ and $Co_4(CO)_{12}$ under comparable conditions for the hydroformylation (eq. 1) and hydroesterification (eq. 2) reactions.



$$RCH{=}CH_2 \xrightarrow[\text{Cat.}]{CO/H_2} RCH_2CH_2CHO + \underset{\substack{|\\ CHO}}{RCHCH_3} \qquad (1)$$



$$RCH{=}CH_2 \xrightarrow[\text{Cat.}]{CO/CH_3OH} RCH_2CH_2COOCH_3 + \underset{\substack{|\\ COOCH_3}}{RCHCH_3} \qquad (2)$$

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Experimental

$Co_2(CO)_8$ and $Co_4(CO)_{12}$ were prepared by standard procedures [7,8] and recrystallized from methylene chloride and toluene, respectively, until no further changes in the IR intensities were observed. Experiments were carried out in magnetically stirred autoclaves. The described effects were only observed when no cobalt metal deposits were present on the wall of the reaction vessel. This was achieved by using either carefully cleaned or glass-coated autoclaves.

Products were analyzed by GLC (Carlo Erba 2150) using n-decane (for hydroformylation) and n-undecane (for hydroesterification) as internal standards on a 100 m × 0.25 mm Ucon LB 550X glass capillary column at 120°C. Immediately before and after the reaction the liquid phase of the reaction mixture was examined by IR spectroscopy (Zeiss IMR 25).

Results

The typical results for the hydroformylation reaction are summarized in Table 1, and those for the hydroesterification in Table 2. Both tables show clearly that $Co_4(CO)_{12}$ is a more active catalyst than $Co_2(CO)_8$. The isomeric distribution of the hydroformylation products is hardly affected by the choice of the starting catalyst. In the hydrocarboxylation a faster isomerization is observed with $Co_4(CO)_{12}$ than with $Co_2(CO)_8$ at temperatures >100°C.

With increasing temperature and prolonged reaction times the gap between the yields of hydroformylation products of the two catalysts narrows (Table 1). From the temperature dependence of the product yields an approximate apparent activation energy of ~140 kJ/mol can be calculated for the hydroformylation and one of ~30 kJ/mol for the hydroesterification. Within the margin of error (±15 kJ/mol) these are independent of which carbonyl complex is used.

TABLE 1

HYDROFORMYLATION OF OCTENE-1 WITH $Co_2(CO)_8$ AND $Co_4(CO)_{12}$

Conditions: p 200 bar, CO/H_2 1/1, concentration of $Co_2(CO)_8$ 0.0148 mol/l [a], concentration of $Co_4(CO)_{12}$ 0.0074 mol/l [a], concentration of octene-1 1.5 mol/l, solvent: toluene.

Catalyst	Temperature (°C)	Reaction time (h)	Yield of aldehyde (mol%)	Isomeric distribution			
				-1 (%)	-2 (%)	-3 (%)	-4 (%)
$Co_2(CO)_8$	60	1	[b]				
$Co_4(CO)_{12}$	60	1	[b]				
$Co_2(CO)_8$	60	16	2.0	77	16	4	3
$Co_4(CO)_{12}$	60	16	7.3	80	15	3	3
$Co_2(CO)_8$	80	1	[b]	—	—	—	—
$Co_4(CO)_{12}$	80	1	9.4	79	15	4	3
$Co_2(CO)_8$	80	7	39	79	15	4	2
$Co_4(CO)_{12}$	80	7	56	79	15	4	3
$Co_2(CO)_8$	100	1	41	78	15	4	3
$Co_4(CO)_{12}$	100	1	74	74	17	5	4

[a] The catalyst concentrations correspond to equivalent amounts of cobalt (= 0.03 mol Co/l), [b] Not possible to determine (<1%).

TABLE 2

HYDROESTERIFICATION OF OCTENE-1 WITH $Co_2(CO)_8$ AND $Co_4(CO)_{12}$

Concentration of $Co_2(CO)_8$ 0.054 mol/l [a], concentration of $Co_4(CO)_{12}$ 0.027 mol/l [a], concentration of octene-1 2.5 mol/l, solvent: methanol

Catalyst	Pressure (Bar)	Temperature (°C)	Reaction time (h)	Yield esters (mol%)	Isomeric distribution of octane carboxylic esters			
					-1 (%)	-2 (%)	-3 (%)	-4 (%)
$Co_2(CO)_8$	75	80	14	10	67	22	6	5
$Co_4(CO)_{12}$	75	80	14	14	67	21	7	5
$Co_2(CO)_8$	75	100	14	14	72	20	6	3
$Co_4(CO)_{12}$	75	100	14	28	61	23	9	7
$Co_2(CO)_8$	75	120	14	14	67	21	8	4
$Co_4(CO)_{12}$	75	120	14	28	52	23	13	12
$Co_2(CO)_8$	250	80	14	18	71	22	5	3
$Co_4(CO)_{12}$	250	80	14	25	71	21	5	3
$Co_2(CO)_8$	250	100	14	24	76	19	4	2
$Co_4(CO)_{12}$	250	100	14	50	69	21	6	4
$Co_2(CO)_8$	250	120	14	39	73	19	5	3
$Co_4(CO)_{12}$	250	120	14	64	61	23	9	8

[a] The catalyst concentrations correspond to equivalent amounts of cobalt (= 0.11 mol Co/l).

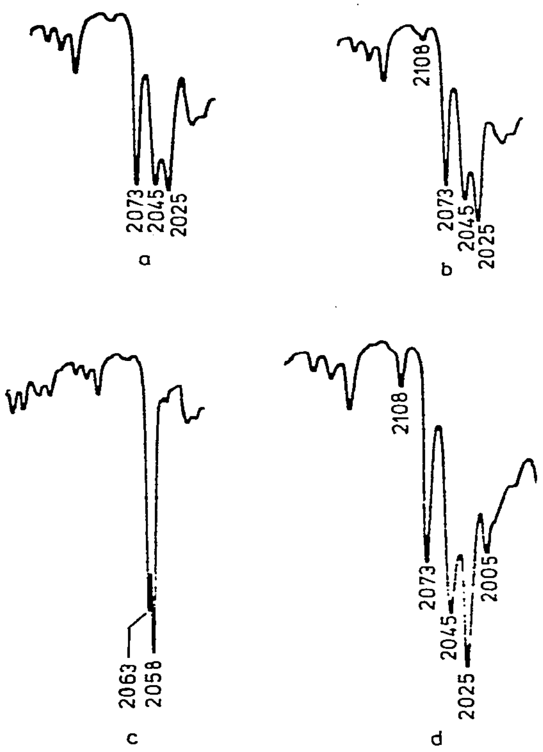

Fig. 1. The IR spectra of the liquid hydroformylation mixture. $Co_2(CO)_8$ before (a) and after (b) reaction. $Co_4(CO)_{12}$ before (c) and after (d) reaction. Reaction conditions: 80°C, 1 h, 200 bar CO/H_2.

Figure 1 shows the infrared spectra of the liquid phase of the reaction mixture before and after the hydroformylation reaction in the region of the terminal CO-bands (~2000 cm^{-1}). The region of the bridging CO (~1800 cm^{-1}) is masked by solvent absorption. The starting solutions show the typical spectra of $Co_4(CO)_{12}$ and $Co_2(CO)_8$ [9,10], the latter being somewhat broadened as compared to the heptane spectrum. At the end of the reaction with $Co_4(CO)_{12}$ the spectrum of the liquid phase is consistent with a mixture of the acyl complex $RCOCo(CO)_4$ and a minor amount of $Co_2(CO)_8$ [12], but no $Co_4(CO)_{12}$ remains. The reaction mixture from the $Co_2(CO)_8$ catalyst contains mainly $Co_2(CO)_8$ and perhaps a small amount of $RCOCo(CO)_4$ and $HCo(CO)_4$.

In the hydroesterification the results are similar to those in the hydroformylation, except that at low temperatures (80°C) the gap between the product yields for $Co_2(CO)_8$ and $Co_4(CO)_{12}$ is smaller than at higher temperatures. The reaction mixture could not be examined by IR spectroscopy because of solvent absorption in the 2000 cm^{-1} region.

Discussion

Any mechanism designed to explain our results must account for two major features: (a) $Co_4(CO)_{12}$ and $Co_2(CO)_8$ show differing catalytic activity in both the hydroformylation and the hydroesterification reaction, and (b) $Co_4(CO)_{12}$ and $Co_2(CO)_8$ seem to produce the same catalytically active intermediates, as indicated by the similar apparent activation energies and product distributions, and by the IR spectra of the reaction mixtures.

Although we are far from understanding this behaviour completely, one obvious explanation would be to assume different concentrations of the catalytically active species over many catalytic cycles. How could this be achieved? Our suggestion for the catalytic cycle at the beginning of the hydroformylation reaction (i.e. low conversions) based on literature data [3,11—14] is summarized in Fig. 2. $Co_2(CO)_8$ reacts with hydrogen to form $HCo(CO)_4$, which must loose one

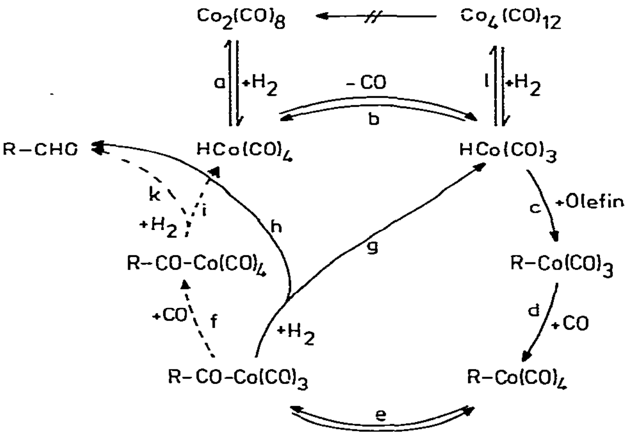

Fig. 2. Catalytic cycle for the hydroformylation reaction using $Co_2(CO)_8$ and $Co_4(CO)_{12}$ as starting catalysts [3,13].

carbon monoxide to form $HCo(CO)_3$, the reactive species capable of complexing the olefin. These reactions a and b are relatively slow, e.g. the half-life of $Co_2(CO)_8$ at 100°C, 25 bar H_2, and 25 Bar CO is about 20 min [16]. Thus it is reasonable to assume that not all of the $Co_2(CO)_8$ is converted into the active complex (e.g. $HCo(CO)_3$) during short reaction times. $Co_4(CO)_{12}$, however, may be capable of adding H_2 to form $HCo(CO)_3$ directly (path 1) with a lower activation barrier than required for steps a + b. This would result in a higher concentration of active catalyst starting from $Co_4(CO)_{12}$. We can exclude a direct, conversion of $Co_4(CO)_{12}$ into $Co_2(CO)_8$, since this process is known to be slow [6], but the hydroformylation with $Co_4(CO)_{12}$ is faster than with $Co_2(CO)_8$.

To explain our results we have to assume that the main catalytic cycle proceeds via path c, d, e, f and g, and that paths h and i are side-tracks. Otherwise all of the catalyst would end up as $HCo(CO)_4$ (or $Co_2(CO)_8$) after one cycle, and the differences between the two complexes would not be explained.

At the beginning of the reaction the intermediate $HCo(CO)_3$ is mainly trapped by the olefin (c). Assuming $Co_4(CO)_{12}$ produces $HCo(CO)_3$ faster than $Co_2(CO)_8$ the higher reaction rate with the $Co_4(CO)_{12}$ catalyst is understandable. During the course of the reaction more and more of the catalyst ends up as $RCOCo(CO)_4$, $HCo(CO)_4$, or $Co_2(CO)_8$, either via the side track (f, i) or via the equilibrium (b). Thus the reactions of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ become more and more equivalent. At higher temperatures the differences between the two complexes also decrease, since now $Co_2(CO)_8$ is activated more easily.

The results for the hydroesterification can be explained along the same lines, with methanol taking the place of H_2 in the displacement reaction (f, g). However side reactions of the catalyst, such as disproportionation [17] and the scarcity of data prevent a detailed discussion of the results.

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