Re-evaluation of the mechanism of the stoichiometric hydroformylation of olefins with cobalt carbonyls as catalysts

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Abstract

Two types of stoichiometric hydroformylation reactions have been described in the literature. One was performed using stoichiometric amounts of $HCo(CO)_4$ as the cobalt complex, and the second using stoichiometric amounts of $Co_2(CO)_8$ at high hydrogen pressure. It has been believed that the second reaction follows the mechanism of the first, once $HCo(CO)_4$ was formed from $Co_2(CO)_8$ and hydrogen. However, there have been some serious discrepancies between the expected mechanism of this reaction and its actual experimental behavior. Using a high pressure–high temperature infrared throughput cell, we have examined in situ whether the second type reaction does indeed proceed as a stoichiometric reaction between $HCo(CO)_4$ and olefin, and hence, in this case, the role of $Co_2(CO)_8$ is merely to activate the hydrogen to form $HCo(CO)_4$, or whether there is some other mechanism which is more appropriate to describe the reaction.

1. Introduction

The hydroformylation reaction, first discovered by Roelen in 1938 [1], was the first important homogeneous transition metal catalyzed reaction. The basic reaction involves the conversion of olefins to aldehydes in the presence of a mixture of carbon monoxide and hydrogen (synthesis gas) using cobalt catalysts. When the aldehyde synthesis is carried out at high temperature and high pressure of synthesis gas with a small quantity of cobalt responsible for converting considerable large amounts of olefin to produce aldehyde, the reaction is purely catalytic. On the other hand, when the aldehyde synthesis is carried out at room conditions using $Co_2(CO)_8$ or $HCo(CO)_4$ in stoichiometric concentrations, the reaction is considered stoichiometric. Despite these differences, it became clear relatively early that the stoichiometric reaction and the catalytic reaction were very closely related and that mechanistic information obtained from the stoichiometric reaction conveniently conducted at room conditions, was applicable to the catalytic reaction [2–5].

The formation and decomposition of $HCo(CO)_4$ was believed to play an important role in the stoichiometric hydroformylation since it has been believed that $HCo(CO)_4$ is the active species in the reaction [6,7], or at least the precursor of the active species, the latter being postulated many times as $HCo(CO)_3$ [7,8]. Indeed, the formation of $HCo(CO)_4$ from $Co_2(CO)_8$ is widely believed to involve electron deficient compounds such as $HCo(CO)_3$ or $Co_2(CO)_7$ [6–10]. Similarly to the stoichiometric hydroformylation, both the formation and the decomposition of $HCo(CO)_4$ are strongly dependent on CO concentration, as suggested by earlier work of Ungváry and Markó [11].
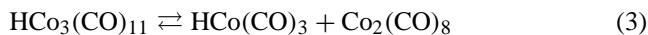
However, later results observed by several groups, showed that the decomposition of $HCo(CO)_4$ to form $Co_2(CO)_8$ is an autocatalytic reaction, i.e., the rate of the reaction increases with the increase in $Co_2(CO)_8$ concentration. Orchin and co-workers [12] suggested that the role of $Co_2(CO)_8$ was to catalyze a reaction that would produce $HCo(CO)_3$, the compound that would further carry on the reaction. Since

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$Co_2(CO)_8$ is very easily transformed to $Co_2(CO)_7$, the reaction sequence would be as follows:

$$Co_2(CO)_8 \rightleftarrows Co_2(CO)_7 + CO \tag{1}$$

$$HCo(CO)_4 + Co_2(CO)_7 \rightleftarrows HCo_3(CO)_{11} \tag{2}$$

$$HCo_3(CO)_{11} \rightleftarrows HCo(CO)_3 + Co_2(CO)_8 \tag{3}$$

Support for this approach was further furnished by Fachinetti et al. [13], who showed that in solutions having high concentrations of $HCo(CO)_4$ and $Co_2(CO)_8$, it is possible to trigger the synthesis of tri-nuclear cobalt carbonyl complexes. The possibility of generating non-negligible amounts of a tri-nuclear cobalt complex during the hydroformylation reaction, when various amounts of $HCo(CO)_4$ and $Co_2(CO)_8$ are constantly present [14], opened the door to new possibilities in formulating a broader understanding of the various mechanistic aspects of the stoichiometric hydroformylation.

Two types of stoichiometric hydroformylation reactions have been described in the literature [10]. One was performed using stoichiometric amounts of $HCo(CO)_4$ as the cobalt complex [6], and the second using stoichiometric amounts of $Co_2(CO)_8$ at high hydrogen pressure [7].

The hydroformylation of olefins carried out with stoichiometric amounts of $HCo(CO)_4$ (Type I), is postulated to proceed according to the mechanism proposed by Kirch and Orchin [6] and Heck and Breslow [8]:

$$HCo(CO)_4 \rightleftarrows HCo(CO)_3 + CO \uparrow$$
$$\overset{>C=C<}{\rightleftarrows} RCo(CO)_3 \overset{+CO}{\rightleftarrows} RCo(CO)_4 \tag{4}$$

$$RCo(CO)_4 \rightleftarrows RCOCo(CO)_3 \overset{+CO}{\rightleftarrows} RCOCo(CO)_4 \tag{5}$$
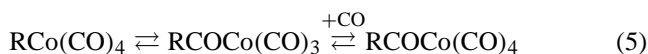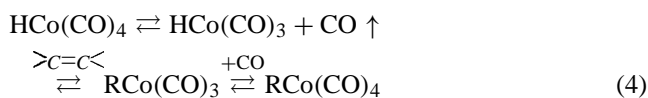
According to Kirch and Orchin, all steps are reversible with the exception of the hydrogenolysis step, which is irreversible. The hydrogenolysis step is postulated in the following way:

$$RCOCo(CO)_4 + HCo(CO)_4 \rightarrow RCHO + Co_2(CO)_8 \tag{6}$$
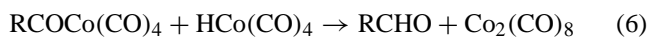
The essential points which characterize this type of stoichiometric hydroformylation are: (a) $HCo(CO)_4$ or $HCo(CO)_3$ are the cobalt complexes which are directly involved in the reaction, both in the step of the reaction with the olefin and also in the hydrogenolysis; (b) the regenerating and recycling cobalt complex is $Co_2(CO)_8$; (c) the hydroformylation rate is strongly dependent on the presence or absence of CO.

The stoichiometric hydroformylation reaction carried out with stoichiometric amounts of $Co_2(CO)_8$ and H_2 (Type II), obeys the following stoichiometry [10]:

$$Co_2(CO)_8 + 2 {>}C{=}C{<} + 2H_2 \rightarrow \tfrac{1}{2}Co_4(CO)_{12} + 2RCHO \tag{7}$$
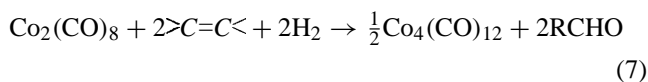
The reaction was carried out under high hydrogen pressure assuming that this high pressure, e.g. 100 atm H_2, is needed to form $HCo(CO)_4$ in the first phase of the reaction [7]. The hydroformylation itself was believed to proceed according to the mechanism described for the $HCo(CO)_4$-mediated reaction, i.e., that once the $HCo(CO)_4$ was formed, the reaction proceeds as a reaction between $HCo(CO)_4$ and olefin. The essential points which characterize this type of hydroformylation are: (a) hydrogen is activated by $Co_2(CO)_8$ in the first phase of the reaction; (b) the hydroformylation is believed to be carried out by $HCo(CO)_4$; (c) $Co_2(CO)_8$, and consequently $HCo(CO)_4$ are the only carbon monoxide sources in the system, and therefore, the end product besides the aldehyde is $Co_4(CO)_{12}$.

However, there are some unsolved problems concerning this type of hydroformylation: (a) an induction period concerning the formation of aldehyde is observed in the presence of CO; (b) whether the reaction does indeed proceed as a stoichiometric reaction between $HCo(CO)_4$ and olefin, and hence, in this case, the role of $Co_2(CO)_8$ is merely to activate the hydrogen to form $HCo(CO)_4$, or whether there is some other mechanism which is more appropriate to describe the reaction.

In order to provide further information about the mechanism of the hydroformylation reaction, we have approached the problem in a new way, in the sense that we first pre-equilibrated the $Co_2(CO)_8$ with H_2 to obtain $HCo(CO)_4$, and only after equilibrium was reached, was the olefin introduced into the system. This enabled us to follow the disappearance of the hydride in the presence of olefin, within the high pressure system we have been using.

2. Experimental method

All experiments were carried out in a similar manner, with various concentrations of the cobalt carbonyl species in the pre-equilibrated solutions, and varying types and amounts of olefins and initial CO partial pressures. The amount of 1.9311 g $Co_2(CO)_8$ (synthesized in-house by the standard method using cobalt acetate tetrahydrate) was dissolved in 650 ml *iso*-octane (Fluka) that was pre-treated with $LiAlH_4$ and redistilled under N_2 atmosphere. The solution was introduced by suction into a 1 l stainless-steel autoclave with exclusion of air. The reaction started when 100 atm of CO/H_2 were pressurized into the system. The carbon monoxide partial pressure was 0.59 atm. The reaction was carried out at 43 °C. A sampling tube reaching the bottom of the reaction autoclave was connected directly to a flow-through high pressure–high temperature infrared cell [15,16]. Before each spectrum was scanned, the cell was flushed with 10–15 ml of fresh solution from the autoclave by opening a discharge valve placed after the cell. After each sampling cycle, the autoclave was re-pressurized with the CO/H_2 gas mixture to maintain constant pressure. When the reaction solution reached equilibrium, it contained 6.723 mmol l^{-1} $HCo(CO)_4$, 1.877 mmol l^{-1} $Co_2(CO)_8$ and 0.378 mmol l^{-1} $Co_4(CO)_{12}$. The total volume of the equilibrated cobalt carbonyl mixture remaining in the autoclave was 565 ml.

Prior to the introduction of the olefin, the reaction mixture was allowed to cool down overnight to reach room temperature.

At this point, 19.5 ml of 1-octene (Fluka) were introduced into the system corresponding to a total olefin concentration of 220 mmol l^{-1}, which in turn, corresponded to an olefin/HCo(CO)$_4$ excess of 34:1. The olefin was pre-treated with a small amount of Na/K amalgam, and redistilled under N$_2$. The gas in the autoclave was flushed out and replaced by 100 atm of H$_2$ only. The amount of CO dissolved in the solution corresponded to 17 mmol. The total pressure was maintained constant in the whole system by simultaneously re-pressurizing the autoclave with H$_2$. The reaction was completed after 140 h at 23 °C. The amount of aldehyde formed corresponded to 22.5 mmol, the isomerization reaction gave rise to 56.6 mmol of 2-octene, and 23.1 mmol of olefin remained unreacted (25.1 mmol of unreacted olefin were removed during sampling). The amount of 1-octane formed as a result of hydrogenation was <2%. At the end of the reaction all cobalt was in the form of Co$_4$(CO)$_{12}$ which reached a concentration of 4.289 mmol l^{-1}.

In hydroformylation experiments conducted at low CO partial pressure, no carbon monoxide was introduced in the initial equilibration of the cobalt carbonyl solution. Some CO evolved during the more extensive formation of Co$_4$(CO)$_{12}$ that occurred in the absence of added CO, generating a CO partial pressure of approximately 0.18 atm, corresponding to a total amount of 1.9 mmol. The reaction was carried out with a 135 ml pre-equilibrated solution containing 4.951 mmol l^{-1} HCo(CO)$_4$, 0.798 mmol l^{-1} Co$_2$(CO)$_8$ and 3.248 mmol l^{-1} Co$_4$(CO)$_{12}$. Four milliliter of 1-octene were introduced into the system, corresponding to a concentration of 195.5 mmol l^{-1}, and to an olefin/HCo(CO)$_4$ excess of 39:1. The reaction was completed after 23 h at 30 °C. The amount of aldehyde formed corresponded to 1.1 mmol, the isomerization reaction gave rise to 20.4 mmol of 2-octene, and 4.8 mmol of olefin remained unreacted.

Infrared spectra were recorded on a Grating Perkin-Elmer Model 325, with a resolution of ~0.9 cm^{-1} and on a Grating Perkin-Elmer Model 983G, microprocessorized with Data Station Model 3600, resolution ~0.5 cm^{-1}.

3. Results and discussion

3.1. The hydroformylation of 1-octene

The experiments were divided into two categories: (a) those performed in the absence of added CO; and (b) those performed in the presence of added CO. In the experiments belonging to the first category, a very low partial pressure was nevertheless present, corresponding to 0.1–0.2 atm, resulting from the thermal decomposition of Co$_2$(CO)$_8$ under H$_2$ pressure, which also generated Co$_4$(CO)$_{12}$ with release of CO. In the experiments carried out in the presence of CO, 0.6–0.8 atm of CO were introduced at the beginning

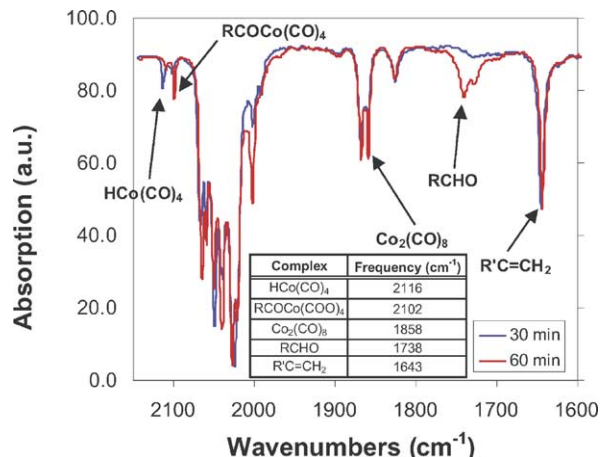Fig. 1. Infrared spectra of the initial stages of the Type II stoichiometric hydroformylation of 1-octene in a pre-equilibrated HCo(CO)$_4$/Co$_2$(CO)$_8$ solution with an olefin:hydride ratio of 34:1.

of the equilibration reaction, before adding the olefin. Apparently, the difference in the CO partial pressure between these two categories is small, but as we shall see from the results obtained, it dramatically affects the course of the reaction, the reaction rate and, as a consequence, the observability of possible intermediates. The progress of the hydroformylation reaction of 1-octene was followed by infrared spectroscopy. Fig. 1 shows some typical infrared spectra of the initial stages of the reaction in which all the important cobalt carbonyl intermediate species are present.

3.1.1. Induction period

The formation of aldehyde after the olefin was introduced into the system proceeded promptly without any induction period, when the CO partial pressure was 0.1 atm, and it started after an induction period of 20 min when CO partial pressure was 0.6 atm. Fig. 2 shows the formation of aldehyde with and without CO. This induction period may, at first sight, be regarded as a retarding effect of CO, a phenomenon that was observed in connection with other reactions of this type. However, we observed that this induction period concerned only the aldehyde formation [17,18]. Actually, during the induction period, a reaction occurs, which
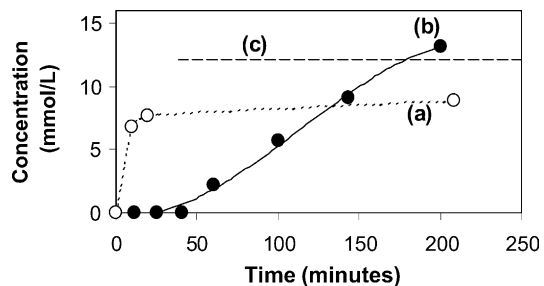

Fig. 2. Formation of aldehyde (1-nonanal): (a) under 0.1 atm CO; (b) under 0.6 atm CO; (c) maximal theoretical aldehyde concentration under conditions as in (a).
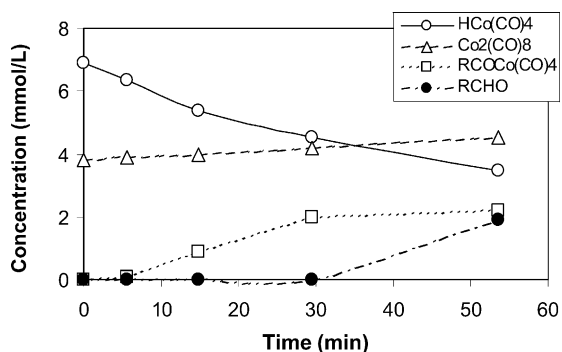
Fig. 3. The induction period observed in the hydroformylation reaction of 1-octene to form 1-nonanal.

causes a decrease in $HCo(CO)_4$ concentration and an increase in $Co_2(CO)_8$ concentration, with no change in the concentrations of other compounds, with exception of the formation of the acyl cobalt tetracarbonyl, $RCOCo(CO)_4$, as shown in Fig. 3. It appears, that the introduction of the olefin causes a break-down of the equilibrium between $Co_2(CO)_8$ and $HCo(CO)_4$ in solution.

3.1.2. Formation of the acyl cobalt tetracarbonyl

The formation of the acyl cobalt tetracarbonyl, followed by its decomposition, was observed in all experiments where 1-octene was used as the olefinic substrate [17,19]. In the presence of 0.6 atm CO, the acyl cobalt complex reached a maximal concentration representing 30% of the total concentration of cobalt carbonyl in solution, while in the presence of only 0.1 atm CO, the acyl cobalt complex reached only 4% of the total concentration of cobalt carbonyls. Fig. 4 shows that the maximal concentration of $C_8H_{17}COCo(CO)_4$ in the presence of 0.6 atm CO is higher than that in the presence of 0.1 atm CO, and that the overall lifetime of the acyl complex in solution is longer in the presence of 0.6 atm CO. It seems that CO is needed in order to enable the formation of the acyl cobalt tetracarbonyl. The initial rate of formation of the $C_8H_{17}COCo(CO)_4$ in the presence of 0.6 atm of carbon monoxide was estimated at 8.5×10^{-7} mol l^{-1} s^{-1}. As we have shown, the formation of the acyl cobalt complex
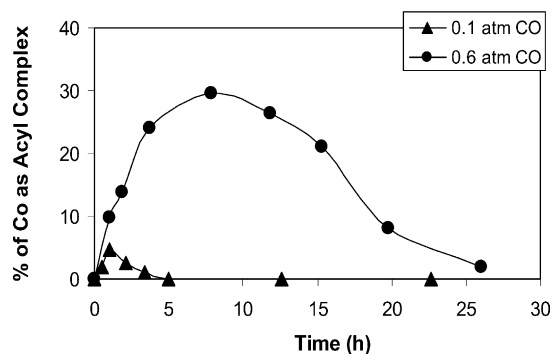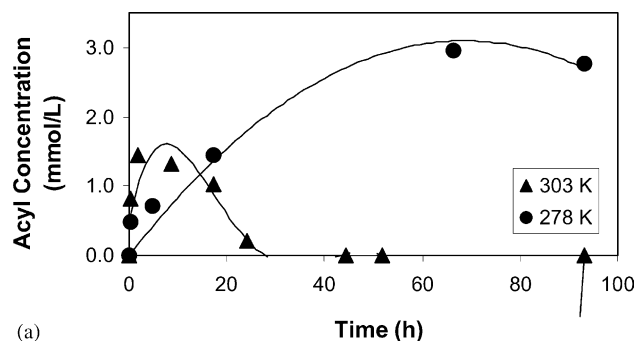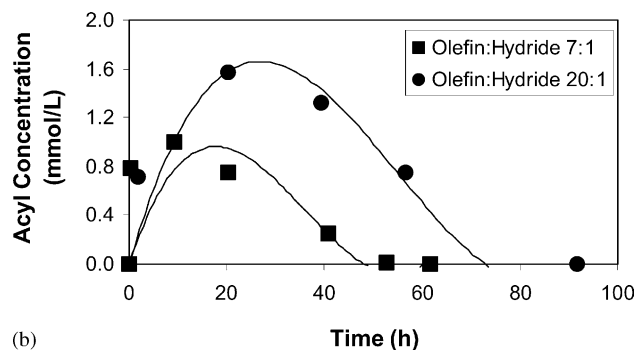

Fig. 4. The formation of the $C_8H_{17}COCo(CO)_4$ acyl cobalt tetracarbonyl complex during the initial stages of the stoichiometric hydroformylation of 1-octene.

Fig. 5. (a) Effect of temperature on the formation of the $C_8H_{17}COCo(CO)_4$ acyl cobalt tetracarbonyl complex in the presence of 0.6 atm CO. (b) Effect of the excess of 1-octene on the formation of the corresponding $C_8H_{17}COCo(CO)_4$ acyl cobalt tetracarbonyl complex in the presence of 0.6 atm CO.

is strongly dependent on CO concentration. However, two other important factors can affect, to a large extent, the formation of the acyl complex. Fig. 5a and b shows the effects of temperature and of the olefin excess on the formation of the acyl complex. It seems plausible that the lower the temperature, the higher the maximum concentration of the acyl complex (Fig. 5a). Apparently, the decomposition reaction of the acyl is slowed down more than the rate of the acyl formation at lower temperature, and hence the acyl can accumulate. It is also possible that at lower temperatures, a favorable entropy change due to the insertion of CO generate a greater accumulation of the cobalt acyl complex. A higher olefin concentration gives rise to a higher acyl cobalt concentration (Fig. 5b), a phenomenon that has also been observed in the Type I stoichiometric hydroformylation reaction.

3.1.3. Formation of $Co_2(CO)_8$

The most striking result obtained in our present work, is that in the presence of olefin, $Co_2(CO)_8$ is formed from $HCo(CO)_4$ and reaches a relatively high concentration that remains stable as long as CO is present in the gas phase, as shown in Fig. 6a and b. We must differentiate between two cases: (a) 0.6 atm CO were initially added, and the equilibrated starting solution consisted of 35% $Co_2(CO)_8$ and 65% $HCo(CO)_4$; (b) No CO was initially added, and the equilibrated starting solution consisted of 52% $HCo(CO)_4$,
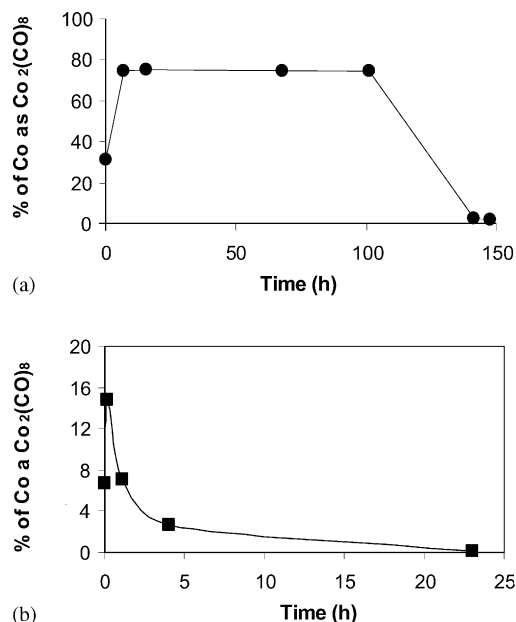
(a)

(b)

Fig. 6. The maximum extent of the concentration of $Co_2(CO)_8$ in solution after the addition of 1-octene and the onset of the hydroformylation reaction. The total amount of 'Co(CO)$_4$' units in solution in this case was 6 mmol. (a) In the presence of 0.6 atm CO; (b) in the presence of 0.1 atm CO.

Table 1
The initial rates of the formation of the aldehyde and the decomposition of $HCo(CO)_4$ for all three olefins used, in the presence and absence of added CO

Substrate	p_{CO} (atm)	$+\left(\dfrac{d[RCHO]}{dt}\right)_{initial}$ (mol l^{-1} s^{-1})	$-\left(\dfrac{d[HCo(CO)_4]}{dt}\right)_{initial}$ (mol l^{-1} s^{-1})
Part A: linear olefins			
1-Octene	0.1	1.5×10^{-5}	0.8×10^{-5}
1-Octene	0.6	2.1×10^{-6}	1.1×10^{-6}
Part B: bulky olefins			
3,3-DMB	0.1	1.5×10^{-6}	1.2×10^{-6}
3,3-DMB	0.6	3.8×10^{-8}	3.3×10^{-8}
Cyclohehene	0.1	0.2×10^{-6}	4.4×10^{-8}
Cyclohehene	0.6	1.3×10^{-8}	5.7×10^{-9}

The reaction conditions were: $pH_2 = 100$ atm, $T = 22$–$23\,°C$, olefin/$HCo(CO)_4 = 40:1$ molar ratio.

8% $Co_2(CO)_8$ and 40% $Co_4(CO)_{12}$, and the CO released during the equilibration reaction corresponded to 0.1 atm in the gas phase. In the presence of 0.1 atm CO, $Co_2(CO)_8$ reaches a maximum concentration representing 15% of total cobalt concentration in the solution. At very low p_{CO} (<0.1 atm), $Co_2(CO)_8$ is unstable and, therefore, a decomposition to $Co_4(CO)_{12}$ occurs. On the other hand, in the presence of added CO, $Co_2(CO)_8$ reaches a maximum concentration representing 74% of total cobalt concentration in solution that remains stable for over 100 h. This increase in $Co_2(CO)_8$ concentration which is more rapid than that corresponding to the reaction $\frac{1}{2}Co_4(CO)_{12} + 2CO \rightarrow Co_2(CO)_8$, may suggest that the reaction proceeds according to the mechanism proposed for the stoichiometric hydroformylation with $HCo(CO)_4$, i.e. hydrogenolysis of the acyl complex is performed by $HCo(CO)_4$ to give aldehyde and $Co_2(CO)_8$. However, since in the case where no initial CO was added the same phenomenon is observed as well, i.e. an increase in the concentration of $Co_2(CO)_8$ is observed, we must rule out the above hypothesis.

3.1.4. Relationships between the formation of aldehyde and the disappearance of $HCo(CO)_4$

A rough evaluation of the initial rate of the disappearance of $HCo(CO)_4$ during the reaction shows that it is slower than the initial rate of formation of the aldehyde regardless of the presence or absence of carbon monoxide. Clearly, the numerical values of the initial rates mentioned above are different with different carbon monoxide concentrations and are shown in Table 1 (Part A).

It is evident, also in this aspect, that in the presence of CO the reaction proceeds more slowly than in the absence of CO. In the latter case, the initial rates both for the formation of the aldehyde and for the decomposition of $HCo(CO)_4$, are approximately one order of magnitude higher than the corresponding initial rates in the presence of CO.

In both cases the initial rate of formation of the aldehyde is about twice that of the disappearance of $HCo(CO)_4$. This fact certainly disagrees with the requirement for the stoichiometric hydroformylation carried out with $HCo(CO)_4$ [6], in which the reaction stoichiometry requires that $HCo(CO)_4$ should disappear at a rate double than the rate of aldehyde formation.

In the presence of CO, the total amount of aldehyde formed during the reaction is almost four times the amount of $Co(CO)_4$ groups present in solution, as shown in Table 2 (e.g., 3.0 mmol of $Co_2(CO)_8$ initially present, and 22.5 mmol of aldehyde formed). The limiting parameter for the formation of the aldehydes seems to be the amount of free carbon monoxide and not only the amount of $Co_2(CO)_8$ available in the reaction system.

Table 2
The amount of cobalt cabonyl complexes in different hydroformylation experiments, expressed as the total number of initial 'Co(CO)$_4$' units, and the corresponding amount of aldehyde formed, both in the presence and absence of added CO

p_{CO} (atm)	Co(CO)$_4$ units (mmol)	Aldehyde (mmol)	Aldehyde (mmol)/Co(CO)$_4$ units (mmol))
0.6	2.9	10.9	3.8
0.6	3.6	13.6	3.8
0.6	5.9	22.5	3.8
0.6	4.3	16.7	3.8
0.1	4.4	5.7	1.3
0.1	0.8	1.1	1.3

The reaction conditions were: $pH_2 = 100$ atm, $T = 22$–$23\,°C$, olefin/$HCo(CO)_4 = 40:1$ molar ratio.

3.1.5. Decrease of $Co_2(CO)_8$ concentration and increase of $Co_4(CO)_{12}$ concentration

The end of the reaction is marked in all cases by a decrease in $Co_2(CO)_8$ concentration, accompanied by the increase in $Co_4(CO)_{12}$ concentration. At the end of the reaction, all cobalt is present as $Co_4(CO)_{12}$ as found in previous experiments of the hydroformylation of olefins with $Co_2(CO)_8$ and hydrogen [7]. When the reaction is carried out in the absence of added carbon monoxide, ($p_{CO} < 0.1$ atm), the concentration of $Co_2(CO)_8$ reaches a maximum after 40 min at room temperature (see Fig. 6b) and then decreases immediately. However, in the presence of 0.6 atm CO, at room temperature (22–23 °C), the maximum concentration of $Co_2(CO)_8$ remains stable for a longer period (see Fig. 6a). During this period, the aldehyde concentration increases, while CO in the gas phase (and the dissolved carbon monoxide in solution, whose concentration is proportional to CO partial pressure in the gas phase) is being consumed. When the partial pressure of carbon monoxide in the gas phase reaches a level, which is not sufficient for the stabilization of $Co_2(CO)_8$, the latter starts to decompose to give $Co_4(CO)_{12}$ and CO, which is then used up in the formation of additional aldehyde. This decomposition process is shown in Fig. 7a and b. During the period of the decomposition of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ and

CO, the aldehyde grows in accordance with the amount of CO molecules released during the '$Co(CO)_4$' $\rightarrow$ '$Co(CO)_3$' transformation.

3.2. Effect of the olefin structure on hydroformylation

The hydroformylation of α-olefins is always accompanied by a large extent of isomerization (formation of 2-octene in the case of 1-octene as the initial substrate), a process that complicates the analysis of the components. Hence, we have chosen for further investigations olefins that either cannot isomerize, such as 3,3-dimethylbutene, or in which the isomerization product is identical with the initial olefin, such as cyclohexene).

3.2.1. Induction period

In the absence of added CO, ($p_{CO} < 0.1$ atm), no induction period was observed with either 3,3-dimethylbutene or cyclohexene. On the other hand, in the presence of 0.6 atm CO, an induction period was observed with both olefins, that was longer than that measured with 1-octene. These results are illustrated in Fig. 8a and b. The nature of the olefin has a strong influence on the length of the induction period, which increases in the following order:

1-octene $\ll$ 3, 3-dimethylbutene $<$ cyclohexene.

With both 3,3-dimethylbutene and cyclohexene, no formation of the acyl cobalt tetracarbonyl is observed, which

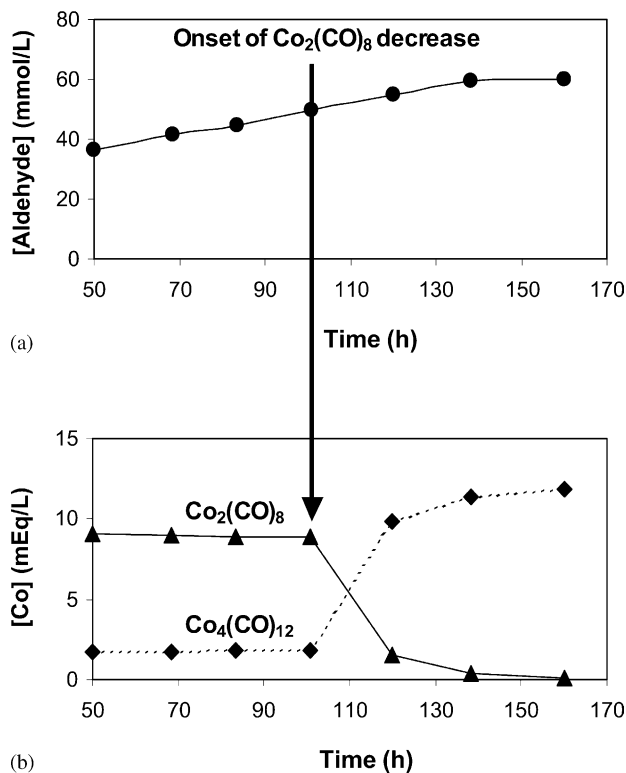Fig. 7. The formation of aldehyde (1-nonanal) during the CO-depleted stage in which $Co_2(CO)_8$ is transformed to $Co_4(CO)_{12}$: (a) increase of aldehyde concentration; (b) increase of $Co_4(CO)_{12}$ concentration and decrease of $Co_2(CO)_8$ concentration. The large arrow from the top portion of the figure shows the extent of aldehyde formed after the onset of the decrease of $Co_2(CO)_8$, which acts at that point as the sole source of CO in the system.
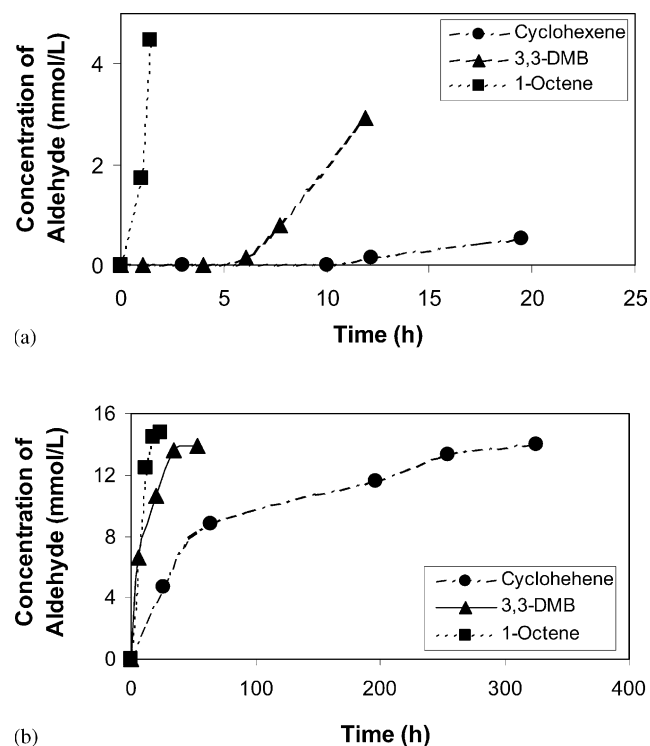

Fig. 8. The Type II stoichiometric hydroformylation reaction with different olefins: (a) in the presence of 0.6 atm CO; (b) in the presence of 0.1 atm CO.

Table 3
The time of reaction necessary to achieve a constant concentration of aldehyde formed in solution and a complete conversion of the cobalt carbonyl complexes to $Co_4(CO)_{12}$

Olefin	p_{CO} (atm)	Time of reaction (h)
1-Octene	0.1	23
1-Octene	0.6	140
3,3-DMB	0.1	44
3,3-DMB	0.6	192
Cyclohexene	0.1	330
Cyclohexene	0.6	>800

The reaction conditions were: $pH_2 = 100$ atm, $T = 22$–$23\,^\circ$C, olefin/ $HCo(CO)_4 = 40$:1 molar ratio.

suggests that the somewhat increased bulkiness of these olefins compared to the 1-octene, causes the acyl complex to be highly unstable, i.e., its rate of formation which might be much lower compared to that from 1-octene, would be similar to its rate of decomposition.

During the induction period, a reaction occurs which causes the increase in $Co_2(CO)_8$ concentration and the decrease in $HCo(CO)_4$ concentration. No other changes in the concentration of other compounds can be observed. As suggested in the case of 1-octene, it seems that, also with other olefins, upon introduction of the olefin into the system, a reaction occurs which produces $Co_2(CO)_8$ and at slow rate a compound that might actually catalyze the hydroformylation reaction.

3.2.2. Initial rates of reaction

A very rough estimation of the initial rates for the formation of the aldehyde and the decomposition of $HCo(CO)_4$ for both 3,3-dimethylbutene (3,3-DMB) and cyclohexene in the presence and absence of CO are given in Table 1 (Part B). It is interesting to note, that in the presence of 0.6 atm CO, the initial rate of aldehyde formation after the induction period, is two-fold higher than the initial rate of $HCo(CO)_4$ disappearance, independently of the olefin used in the reaction. However, the initial rates become numerically smaller with increasing bulkiness of the olefins according to the following ordering of the olefins:

1-octene > 3, 3-dimethylbutene > cyclohexene.

The above ordering of the olefins is preserved also in the case of the reaction time (i.e. the time until the concentration of the aldehyde remains constant and the cobalt is present as $Co_4(CO)_{12}$ only), as shown in Table 3. In all cases, regardless of the olefin used, there is a clear "slowing down" effect caused by the presence of carbon monoxide in the system.

3.3. Proposed new alternative mechanism

The initial hypothesis regarding the Type II stoichiometric hydroformylation mechanism was that upon inserting the olefin into the pre-equilibrated $HCo(CO)_4/Co_2(CO)_8/H_2$

system, we should observe a reaction which would actually be a stoichiometric reaction between the hydride and the olefin. If this hypothesis had been true, it would have meant that in the stoichiometric hydroformylation with $Co_2(CO)_8$, the hydride is an intermediate in the reaction, and the only difference between this reaction and the Orchin type reaction (Type I) is that it starts from a different precursor. This would also have implied that the mechanisms of both reactions are identical, and that $HCo(CO)_4$ is the actual active species in the reaction.

The catalytic cycle which we propose should explain all the phenomena that are observed during the course of the reaction: (a) induction period for the formation of the aldehyde; (b) increase in the concentration of $Co_2(CO)_8$ during the induction period; (c) decrease of $HCo(CO)_4$ during the induction period; (d) formation of $RCOCo(CO)_4$ in some cases (with 1-octene); (e) no observed induction period at very low CO pressure (0.1 atm); (f) induction period length dependent on the olefinic substrate; and (g) formation of $Co_4(CO)_{12}$ at the end of the reaction.

The proposed overall mechanism incorporates the various aspects of the individual reaction steps, as shown in Scheme 1. The main characteristics of this mechanism are: (a) the active catalytic species is of the type $H_xCo_y(CO)_z$, which in this particular case could be $HCo_3(CO)_9$; (b) the olefin undergoes direct interaction with the active catalytic species to form a π-complex. This complex can undergo a fast π–σ rearrangement to form a polynuclear alkyl complex. This complex can either react with $HCo(CO)_4$ (when the latter is present in a relatively large amount) to form an alkane, $Co_2(CO)_8$ and hydrogen, or it can react with CO to give a polynuclear acyl complex; (c) the activation of molecular hydrogen can be performed either by a mononuclear alkyl or acyl cobalt carbonyl complex, or by a complex containing more cobalt atoms and thus having the ratio $4 > CO/Co \geq 3$ such as a polynuclear acyl complex; (d) the CO used for the formation of the aldehyde comes probably from the gas phase. When the CO in the gas phase has been consumed, the $Co_2(CO)_8$ present in solution is destabilized and, as a consequence, it will lose CO to form $Co_4(CO)_{12}$; (e) at the end of the reaction, the cobalt is recovered quantitatively as $Co_4(CO)_{12}$. Besides being the product of the decomposition of $Co_2(CO)_8$, $Co_4(CO)_{12}$ may also form from $H_xCo_y(CO)_z$, via the following reaction [14]:

$$H_xCo_y(CO)_z \rightarrow \tfrac{x}{2}H_2 + \tfrac{y}{4}Co_4(CO)_{12} + (z - 3y)CO \qquad (8)$$
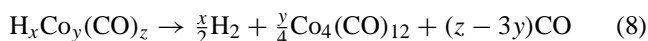
We shall now examine how this proposed overall mechanism helps clarify the various experimental inconsistencies encountered during the various steps of the Type II stoichiometric hydroformylation reaction.

The main features which characterize the induction period observed in our experiments are the following: (a) the introduction of olefin triggers the onset of a reaction that results in a decrease in the $HCo(CO)_4$ concentration, and, contrary to equilibrium requirements, an increase in $Co_2(CO)_8$ concentration. (b) During the induction period, no aldehyde is
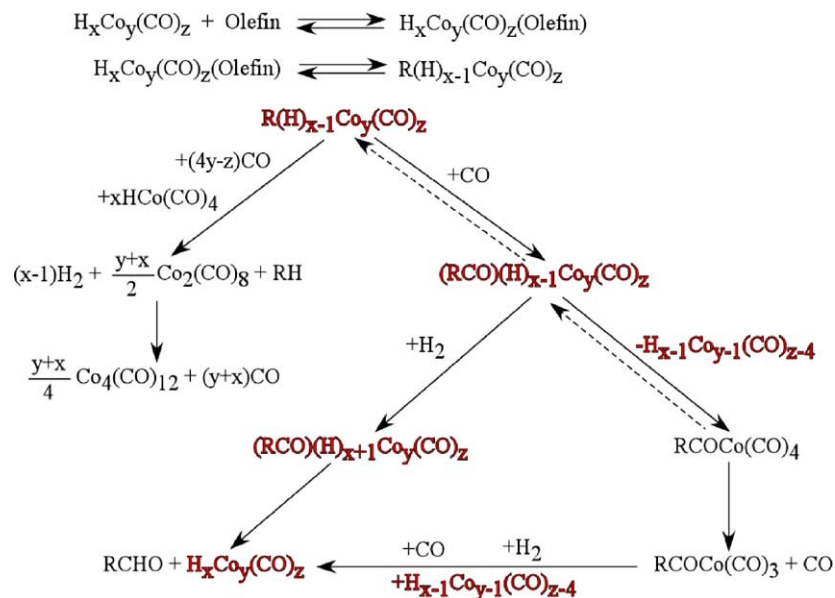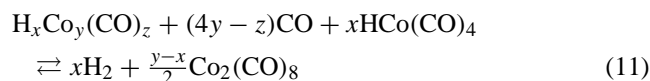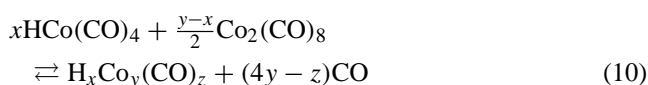
Scheme 1. Overall, generalized proposed mechanism for the stoichiometric hydroformylation reaction. The compounds highlighted in bold letters constitute the pathway of the multi-nuclear cobalt intermediates (most likely tri-nuclear cobalt complexes).

formed. This observation was also made by Pino et al. [7] and at the time not quite understood. (c) The duration of the induction period is strongly dependent on the nature of the olefin, i.e., the bulkier the olefin, the longer the induction period. (d) When the olefin used is 1-octene, a reaction which gives rise also to the formation of the acyl cobalt tetracarbonyl occurs. (e) The induction period is strongly dependent on the CO present in the system, indicating that the mechanism of this reaction must involve coordinatively unsaturated cobalt species.

It is important to remember, that in the pre-equilibrated solution used for the Type II stoichiometric hydroformylation, the $HCo(CO)_4/Co_2(CO)_8/H_2$ system is not the only equilibrium reaction that takes place. The postulation of a trinuclear cobalt complex is not without precedent in the literature. Fachinetti et al. and Fachinetti [20,21] reported that the complex $HCo_3(CO)_9$ readily hydroformylates propylene at temperature as low as $-20\,^\circ$C. Moreover, such a tri-nuclear complex may be formed from $HCo(CO)_4$ and $Co_2(CO)_8$ in the absence of olefin by merely evacuating the reaction vessel several times [13,14]. The reaction for the formation of such a tri-nuclear complex can be represented as follows:

$$HCo(CO)_4 + Co_2(CO)_8 \rightleftarrows HCo_3(CO)_9 + 3CO \qquad (9)$$

Bearing this example in mind, we may suppose that the decomposition of $HCo(CO)_4$ to give $Co_2(CO)_8$ and hydrogen might proceed, among several other mechanism possible, also in the following way:

$$xHCo(CO)_4 + \tfrac{y-x}{2}Co_2(CO)_8$$
$$\rightleftarrows H_xCo_y(CO)_z + (4y - z)CO \qquad (10)$$

$$H_xCo_y(CO)_z + (4y - z)CO + xHCo(CO)_4$$
$$\rightleftarrows xH_2 + \tfrac{y-x}{2}Co_2(CO)_8 \qquad (11)$$

When we add these two reactions, we obtain the net reaction:

$$2xHCo(CO)_4 \rightleftarrows xH_2 + xCo_2(CO)_8 \qquad (12)$$
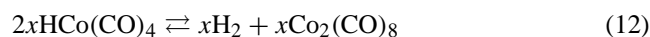
The introduction of an olefin into such a solution causes the destruction of the equilibrium. This breakdown of the equilibrium can be achieved only if the olefin reacts directly with one of the cobalt carbonyl species involved in one of the above equilibrium reactions. We must rule out the hypothesis that a shift in the equilibrium occurs due to a change in the nature of the solvent caused by the addition of the olefin, since the olefin represents only 4% of the solvent, and studies of the reaction between $Co_2(CO)_8$ and hydrogen in benzene [22,23] gave similar results to studies of the same reaction carried out in saturated hydrocarbons [15,22].

We propose, therefore, that the following reaction occurs upon introduction of the olefin:

$$H_xCo_y(CO)_z + \text{olefin} \rightleftarrows H_xCo_y(CO)_z(\text{olefin}) \qquad (13)$$

The new complex formed with the olefin will rapidly undergo a rearrangement:

$$H_xCo_y(CO)_z(\text{olefin}) \rightleftarrows R(H)_{x-1}Co_y(CO)_z \qquad (14)$$
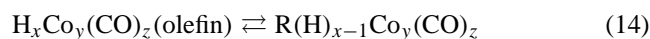
The polynuclear alkyl cobalt carbonyl will further react according to two main reaction pathways, as shown in Scheme 2.

As long as a large concentration $HCo(CO)_4$ is present in the reaction mixture, the polynuclear alkyl will probably react faster with $HCo(CO)_4$ to give $Co_2(CO)_8$, a saturated
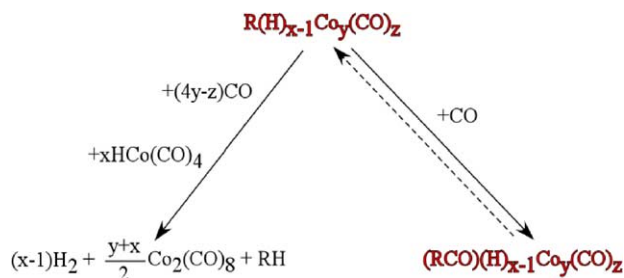
Scheme 2. The two proposed pathways for the reaction of the polynuclear alkyl cobalt carbonyl. The polynuclear complexes are highlighted in bold letters.

hydrocarbon and hydrogen. In the first phase of the reaction after the introduction of the olefin, the reaction of the polynuclear alkyl with $HCo(CO)_4$ will prevail. By postulating a polynuclear alkyl, we also imply that the ratio between the number of moles of $Co_2(CO)_8$ formed this way and the number of moles of RH, be ≥ 2. This may explain why during the induction period a well detectable amount of $Co_2(CO)_8$ is formed, while probably only a small amount of RH is formed. When the concentration of $HCo(CO)_4$ in solution will substantially decrease, the second reaction will start to successfully compete with the reaction of the polynuclear alkyl with $HCo(CO)_4$, and the polynuclear acyl cobalt complex will start to form [24–28].
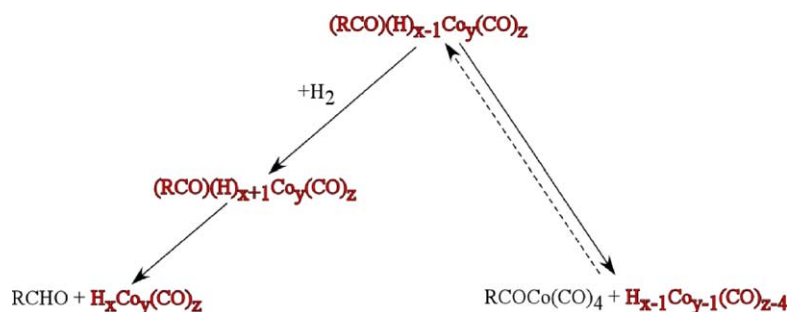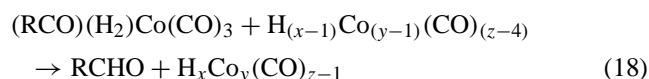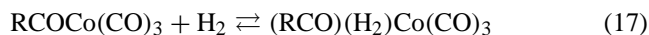
The mechanism explaining the induction period and the increase in $Co_2(CO)_8$ concentration which we propose, can also give a possible explanation to our observation that the nature of the olefin introduced into the system influences a great deal the duration of the induction period. Since both 3,3-dimethylbutene and cyclohexene are somewhat bulkier olefins than 1-octene, it could be that the formation of a polynuclear acyl from a polynuclear alkyl will be slower for 3,3-dimethylbutene and cyclohexene than for 1-octene. The formation of the $C_8H_{17}COCo(CO)_4$ complex, when hydroformylation is carried out with 1-octene, is to our opinion, a side reaction, as shown in Scheme 3. The polynuclear acyl complex, may, especially in the presence of CO, decompose to the acyl cobalt tetracarbonyl, which we detect in our system concomitantly with a decrease in CO concentration in the gas phase, and to some other cobaltcarbonyl species. The

acyl cobalt tetracarbonyl can further react with molecular hydrogen to give the aldehyde. In this case, we can explain the fact that with 3,3-dimethylbutene and cyclohexene, we do not observe the formation of the corresponding acyl complex by arguing that since the formation of the polynuclear acyl is slowed down according to the type of olefin used, the reaction of the acyl cobalt tetracarbonyl with molecular hydrogen will become successfully competitive with its own formation, and hence there will be no possibility for the acyl cobalt tetracarbonyl to accumulate.

The hydrogenolysis step in the Type II stoichiometric hydroformylation reaction has been shown to occur by molecular hydrogen and not by $HCo(CO)_4$, as evidenced by the results obtained in isotope exchange experiments, in which the ratio of the aldehyde products, RCHO and RCDO, corresponded to the ratio of H_2 and D_2 in the gas phase, and not to the ratio of $HCo(CO)_4$ and $DCo(CO)_4$ in solution [17,29]. Moreover, in many experiments where the formation of the acyl was detected, the acyl complex survived in the solution longer than the hydride, while the formation of aldehyde continued to take place. It is impossible to assume that hydride was reformed from $Co_2(CO)_8$ and hydrogen, because at room temperature and in the presence of 0.6 atm CO, the initial rate of formation of the hydride is in the range of 10^{-8} to 10^{-9} mol l^{-1} s^{-1}, which cannot account for the rapid formation of the aldehyde that in the case of 1-octene, has an initial rate of 10^{-5} to 10^{-6} mol l^{-1} s^{-1}. In view of the evidence given above, we propose the following mechanism for the activation of hydrogen:

$$(RCO)(H)_{x-1}Co_y(CO)_z + H_2 \rightarrow RCHO + H_xCo_y(CO)_z$$
$$(15)$$
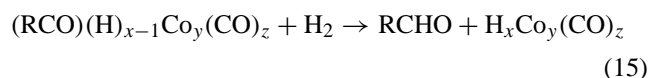
According to this reaction, the active catalytic species will be directly regenerated. Another pathway for the activation of hydrogen can be carried out by $(RCO)Co(CO)_4$:

$$RCOCo(CO)_4 \rightleftharpoons RCOCo(CO)_3 + CO \qquad (16)$$

$$RCOCo(CO)_3 + H_2 \rightleftharpoons (RCO)(H_2)Co(CO)_3 \qquad (17)$$

$$(RCO)(H_2)Co(CO)_3 + H_{(x-1)}Co_{(y-1)}(CO)_{(z-4)}$$
$$\rightarrow RCHO + H_xCo_y(CO)_{z-1} \qquad (18)$$

Scheme 3. The formation of the acyl cobalt tetracarbonyl intermediate as a side reaction resulting from the decomposition of a polynuclear acyl cobalt complex. The polynuclear complexes are highlighted in bold letters.

$$H_xCo_y(CO)_{z-1} + CO \rightleftarrows H_xCo_y(CO)_z \qquad (19)$$

Involving a molecule of the type $H_{(x-1)}Co_{(y-1)}(CO)_{(z-4)}$ and CO, the active catalytic species can be regenerated.

In a stoichiometric reaction of the type Orchin has studied (Type I), a direct reaction is postulated between the hydride and the olefin. The important characteristic of this type of stoichiometric reaction is that 1 mol of $HCo(CO)_4$ reacts with 1 mol of olefin to give 1 mol of acyl, and further, 1 mol of acyl reacts with 1 additional mol of $HCo(CO)_4$ to give 1 mol of aldehyde. Hence, in this type of reaction, 2 mol of the hydride will disappear and 1 mol of aldehyde will be generated. On the basis of this observation, we expected that a stoichiometric hydroformylation, using pre-formed $HCo(CO)_4$ prior to olefin insertion, would show the same characteristic, i.e., the rate of disappearance of $HCo(CO)_4$ would correspond to the rate of formation of the aldehyde. However, this is not the case. The numerical values listed in Table 1 clearly show that the initial rate of disappearance of $HCo(CO)_4$ (after the induction period) is half of the initial rate of formation of the aldehyde. The conclusion which can be drawn from these values is that there is no correspondence between the disappearance of $HCo(CO)_4$ and the formation of the aldehyde. In this case, the Type II reaction is certainly not a reaction between $HCo(CO)_4$ and olefin, and hence $HCo(CO)_4$ is not involved in the aldehyde formation. Therefore, we may conclude that: (a) $HCo(CO)_4$ is not involved also in either the first step of the hydroformylation or in the hydrogenolysis step; and (b) the assumption that $HCo(CO)_4$ is an intermediate in the hydroformylation reaction carried out with $Co_2(CO)_8$ is not correct. The reaction with $Co_2(CO)_8$ proceeds through another mechanism which has very little in common with the Orchin-type mechanism for the Type I stoichiometric hydroformylation.

It became apparent during our experiments that in the case where the system contained 0.6 atm CO (which in our system represented some 17 mmol carbon monoxide), the amount of aldehyde formed during the reaction was 3–4-fold higher than the total amount of $Co(CO)_4$ cobalt carbonyl units present. Table 2 shows the amount of cobalt carbonyls in different experiments, expressed as the number of moles of '$Co(CO)_4$' units and the corresponding amount of aldehyde formed. The hydroformylation reaction in our system generates aldehyde in amounts greatly in excess of the amount expected had the reaction been a pure stoichiometric one. Even when the CO present in the system is only 0.1 atm (due to some decomposition of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ during the initial equilibration of the carbonyl solution), the amount of aldehyde obtained is still 30% higher than expected.

4. Conclusions

In this paper, we attempted to settle some unsolved discrepancies regarding the mechanistic aspects of the Type II stoichiometric hydroformylation, in which $Co_2(CO)_8$ is used as the cobalt carbonyl precursor in the presence of H_2. This type of hydroformylation was believed to proceed according to the mechanism described for the $HCo(CO)_4$-mediated stoichiometric reaction, and once $HCo(CO)_4$ was formed, the reaction would follow the same pathway as the Type I reaction. The essential characteristics of this reaction would have been the activation of H_2 by $Co_2(CO)_8$ in the first phase of the reaction, followed by the stoichiometric reaction of $HCo(CO)_4$ with the olefin to yield aldehyde and $Co_4(CO)_{12}$. However, in situ experimental results show the presence of an induction period in the formation of aldehyde and an unexpected increase in the concentration of $Co_2(CO)_8$ for most of the reaction duration. Hence, the question was posed whether the reaction does indeed proceed as a stoichiometric reaction between $HCo(CO)_4$ and olefin, and hence, in this case, the role of $Co_2(CO)_8$ is merely to activate the hydrogen to form $HCo(CO)_4$, or whether there is some other mechanism which is more appropriate to describe the reaction.

Our results lead us to believe that the hydroformylation reaction with $Co_2(CO)_8$ is not stoichiometric but rather catalytic in nature. This conclusion explains the lack of correlation between the initial rates of formation of the aldehydes and the disappearance of $HCo(CO)_4$. The various cobalt carbonyl complexes whose concentrations have been monitored during the different stages of the reaction, are not directly involved in the catalytic cycle but constitute precursors to the actual catalytic species.

We propose, therefore, that the catalytic cycle best suited to explain all the intriguing phenomena that are observed during the course of the reaction involves the postulation of a polynuclear cobalt carbonyl catalytic species of the type $H_xCo_y(CO)_z$. Such a complex can easily interact with an olefin to form a π-complex that can further undergo a fast π–σ rearrangement to form a polynuclear alkyl complex. This complex, in turn, can either react with $HCo(CO)_4$ to form an alkane, $Co_2(CO)_8$ and hydrogen, or it can react with CO to give a polynuclear acyl complex. The versatility of possible reactions intrinsically associated with such a polynuclear complex is an essential element in understanding various aspect of the mechanism of the stoichiometric hydroformylation. The evidence that we have offered for the involvement of a polynuclear cobalt complex as the catalytic specie is at best circumstantial. Further in situ studies are necessary in light of the new experimental results and the new mechanistic approach, in order to elucidate the actual mechanism of the reaction.

Acknowledgements

References

[1] O. Roelen, Ger. Pat. No. 849,548 (1938); Chem. Zentr. (1953) 927.
[2] M. Orchin, L. Kirch, I.J. Goldfarb, J. Am. Chem. Soc. 78 (1956) 5450.
[3] L. Kirch, M. Orchin, J. Am. Chem. Soc. 80 (1958) 4428.
[4] F. Ungváry, Coord. Chem. Rev. 213 (2001) 1.
[5] I. Wender, S. Metlin, S. Ergun, H.W. Sternberg, H. Greenfield, J. Am. Chem. Soc. 78 (1956) 5401.
[6] L. Kirch, M. Orchin, J. Am. Chem. Soc. 81 (1959) 3597.
[7] P. Pino, R. Ercoli, F. Calderazzo, Chim. Ind. (Milan) 37 (1955) 782.
[8] R.F. Heck, D.S. Breslow, J. Am. Chem. Soc. 83 (1961) 4023.
[9] M. Orchin, W. Rupilius, Catal. Rev. 6 (1972) 85.
[10] I. Wender, P. Pino, Organic Synthesis via Metal Carbonyls, vol. 2, John Wiley & Sons, New York, 1977, p. 47–53.
[11] F. Ungváry, L. Markó, J. Organometal. Chem. 20 (1969) 205.
[12] P. Werner, B.S. Ault, M. Orchin, J. Organometal. Chem. 162 (1978) 189.
[13] (a) G. Fachinetti, L. Balocchi, F. Secco, M. Venturini, Angew. Chem. 93 (1981) 215;
(b) G. Fachinetti, L. Balocchi, F. Secco, M. Venturini, Angew. Chem. Int. Ed. Engl. 20 (1981) 204.
[14] R. Tannenbaum, G. Bor, J. Organometal. Chem. 586 (1999) 18.
[15] R. Tannenbaum, U.K. Dietler, G. Bor, F. Ungváry, J. Organometal. Chem. 570 (1998) 39.
[16] R. Tannenbaum, U.K. Dietler, G. Bor, Inorg. Chim. Acta 154 (1988) 109.
[17] P. Pino, A. Major, F. Spindler, R. Tannenbaum, G. Bor, I.T. Horvath, J. Organometal. Chem. 417 (1991) 65.
[18] M. Beller, B. Cornils, C.D. Frohning, C.W. Kohlpainter, J. Mol. Catal. A: Chem. 1049 (1995) 17.
[19] G. Bor, G. Fachinetti, C.D. Hoff, G. Pályi, C. Zucchi, F. Ungváry, R. Tannenbaum, Inorg. Chim. Acta 353 (2003) 168.
[20] (a) G. Fachinetti, S. Pucci, P.F. Zanazzi, U. Methong, Angew. Chem. 91 (1979) 657;
(b) G. Fachinetti, S. Pucci, P.F. Zanazzi, U. Methong, Angew. Chem. Int. Ed. Engl. 18 (1979) 619.
[21] G. Fachinetti, J. Chem. Soc. Chem. Commun. (1979) 397.
[22] R. Iwanaga, Bull. Chem. Soc. Jpn. 35 (1962) 774.
[23] F. Ungváry, J. Organometal. Chem. 36 (1972) 363.
[24] I. Kovács, F. Ungváry, Coord. Chem. Rev. 161 (1997) 1.
[25] M. Orchin, Acc. Chem. Res. 14 (1981) 259, and references therein.
[26] Z. Nagy-Magos, G. Bor, L. Markó, J. Organometal. Chem. 14 (1968) 205.
[27] C. Zucchi, A. Cornia, R. Boese, E. Kleinpeter, H. Alper, G. Pályi, J. Organometal. Chem. 586 (1999) 61.
[28] S.M. Massik, J.G. Rabor, S. Elbers, J. Marhenke, S. Bernhard, J.R. Schoonover, P.C. Ford, Inorg. Chem. 39 (2000) 3098.
[29] R. Tannenbaum, G. Bor, Organometallics, 2003, in press.