ON THE MECHANISM OF THE $Co_2(CO)_8$ CATALYZED HYDROFORMYLATION OF OLEFINS IN HYDROCARBON SOLVENTS. A HIGH PRESSURE UV AND IR STUDY

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Summary

High pressure IR and UV spectroscopic experiments confirm the Heck and Breslow mechanism of the hydroformylation of 1-octene and cyclohexene with $Co_2(CO)_8$ as the starting catalyst. The major repeating unit is $HCo(CO)_4$, which is formed via the reaction of acylcobalt tetracarbonyl with H_2. The rates are 6.7×10^{-4} mol l^{-1} min^{-1} and 8.8×10^{-5} mol l^{-1} min^{-1} for 1-octene and cyclohexene, respectively at 80°C and 95 bar $CO/H_2 = 1$ in methylcyclohexane. The alternative reaction of $RCOCo(CO)_4$ with $HCo(CO)_4$ is only a minor pathway, with rates of 1.8×10^{-5} mol l^{-1} min^{-1} and 1.1×10^{-5} mol l^{-1} min^{-1} for 1-octene and cyclohexene, respectively. It represents an exit from the catalytic cycle. The activation of the catalyst precursor $Co_2(CO)_8$ is the slowest step of the reaction.

Introduction

The hydroformylation of olefins is one of the most important industrial homogeneous catalytic processes [1,2].

$$RCH=CH_2 + CO + H_2 \xrightarrow[\text{catalyst}]{P,T} RCH_2CH_2CHO + R\underset{\underset{CHO}{|}}{C}HCH_3$$
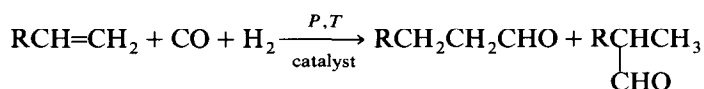
It was soon recognized that with cobalt catalysts, $HCo(CO)_4$ is the active species [3–5]. On the basis of product studies and stoichiometric experiments under normal pressure, a mechanism was developed which is widely accepted today (see Scheme 1) [6]. This mechanism has been tested by in situ IR spectroscopy, but with contradictory results. Whyman observed $Co_2(CO)_8$ and the acyl complex $RCOCo(CO)_4$ during the hydroformylation of 1-octene, and in the case of cyclohexene he observed $Co_2(CO)_8$ and $HCo(CO)_4$ [7]. He concluded that for terminal olefins the reaction of the acyl complex limits the rate of product formation. For internal olefins the slowest step was suggested to be the reaction of $HCo(CO)_4$ with the olefin.
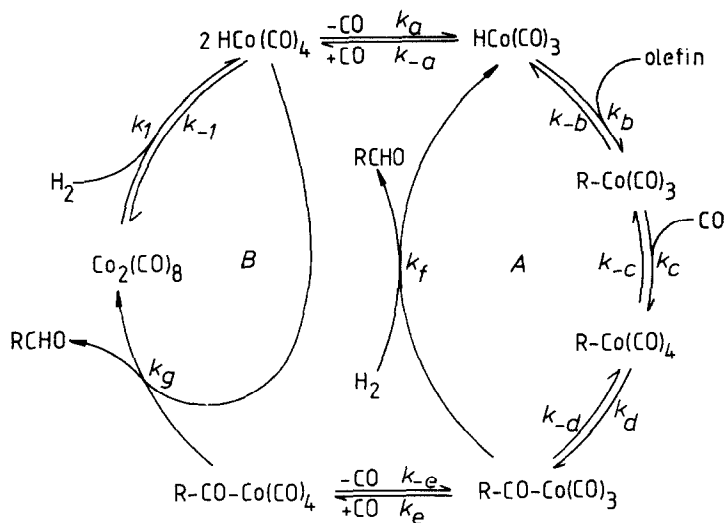
SCHEME 1. Mechanism of the cobalt carbonyl catalyzed hydroformylation (according to R.F. Heck and D.S. Breslow [6]).

Alemdaroglu [8–10] described similar experiments, but reached more quantitative conclusions. He found that $HCo(CO)_4$ is present during the hydroformylation of terminal olefins and questioned Whyman's results. In contrast to earlier reports [11,12] he concluded that the formation of $HCo(CO)_4$ from $Co_2(CO)_8$ is faster than formation of the aldehyde, and that the product formation occurs exclusively via a reaction of the acyl complex with $HCo(CO)_4$. Thus, the repeating unit in his mechanism is $Co_2(CO)_8$ and not $HCo(CO)_4$, as generally assumed [6,13,14]. Some other investigators supported Alemdaroglu's conclusions [15–17].

An alternative mechanism via $Co(CO)_4$ radicals, which is important in the reaction of $HCo(CO)_4$ with some aromatic olefins [18,19], does not contribute to the hydroformylation of aliphatic olefins [20].

In the light of the conflicting results of Whyman's and Alemdaroglu's high pressure IR studies and the importance of the hydroformylation reaction, it seemed of interest to reinvestigate this reaction with the more sophisticated equipment available to us. Our high pressure UV and IR spectroscopy set-up eliminates the problems of warm up periods and mixing encountered in earlier studies, and allows quantitative determination of the cobalt carbonyl species.

Experimental

The experiments were performed in a circulating system consisting of a 1 l autoclave, equipped with electrical heating and a magnetically driven vertically-moving stirrer with a piston pump, a high pressure UV cell with quartz windows in a Cary 118 UV/VIS spectrometer, a high pressure IR cell with CaF_2 windows in a Zeiss IMR-25 IR spectrometer, and a by-pass which allowed us to add additional compounds under pressure [21]. The optical pathlength of the UV cell was 0.05 cm and that of the IR cell 0.009 cm. The temperature of the high pressure cells was kept constant at 25°C in order to ensure a constant ratio of the $Co_2(CO)_8$ isomers with

TABLE 1

IR AND UV DATA FOR THE QUANTITATIVE ANALYSIS OF SPECTRA UNDER HYDROFOR-
MYLATION CONDITIONS [a]

Compound	IR band (cm^{-1})	Extinction coeff. (l mol^{-1} cm^{-1})	Remarks
$Co_2(CO)_8$	1856	1800	
	2032	3600	
	2069	5500	
UV	350 nm	5500	[b]
$HCo(CO)_4$	2032	8100	[c]
$RCOCo(CO)_4$	2003	2740	[d]
1-Octene	1645	33	[e]
Cyclohexene	1655	8.7	[e]

[a] The absolute values of the extinction coefficients may vary by ±15%, depending on the reaction conditions, the choice of the baseline, purity of $Co_2(CO)_8$ etc. For a discussion see for instance refs. 25 and 26. [b] From G.L. Geoffroy and M.S. Wrighton, Organometallic Photochemistry, Academic Press, New York 1979. [c] Calculated on the assumption that the conversion of $Co_2(CO)_8$ to $HCo(CO)_4$ occurs without side reactions at 80°C and 95 bar CO/H_2. The absorption of $Co_2(CO)_8$ at this wavenumber is subtracted when the $HCo(CO)_4$ concentration is calculated. [d] Calculated on the assumption that after the addition of 1-octene, any cobalt not found as $Co_2(CO)_8$ or $HCo(CO)_4$ is present as the acyl complex. [e] Determined from a calibrated curve.

bridged and terminal CO's. The equilibrium between $Co_2(CO)_8$ and $HCo(CO)_4$ changes by < 1% during the time required for the solution to reach the cells (1 to 3 min), and this change is insignificant.

In a typical run the autoclave was charged with 600 ml of argon saturated methyl cyclohexane and 10 ml of decane as GC standard. 1.55 g $Co_2(CO)_8$ and 80 ml olefin were placed in two seperate pressure-stable reservoirs in the by-pass. The system was flushed twice with 10 bar of CO, then the required H_2 and CO pressures were applied. The autoclave was heated to 80°C, then the by-pass was opened and the $Co_2(CO)_8$ was pumped into the autoclave. The conversion of $Co_2(CO)_8$ into $HCo(CO)_4$ was monitored by recording the spectra of the mixture. After the equilibrium was reached (~ 24 h) the olefin was added and the solution was again monitored spectroscopically.

For quantitative analysis the optical densities of the bands were used along with a calibration curve. The absorptivities obeyed Beer's law. The absorption bands listed in Table 1 were used for the analysis.

The organic reaction products were analyzed by gas chromatography (200 m UCON LB 550 × glass capillary, oven temperature programmed 15 min at 60°C, then 10°C min^{-1} to 150°C, carrier 2 bar N_2, FI-detector).

$Co_2(CO)_8$ was prepared by standard procedures [23]. 1-Octene and cyclohexene (EGA) were tested for peroxides, and the tests being negative, were used without further treatment.

Results

The hydroformylations of 1-octene and cyclohexene were studied at 80°C and at 95 bar of synthesis gas pressure ($CO/H_2 = 1$). The liquid phase was continuously pumped through a high pressure UV and a high pressure IR cell. IR and UV spectra were recorded at appropriate intervals.

TABLE 2

KINETIC PARAMETERS FOR THE HYDROFORMYLATION OF 1-OCTENE AND CYCLOHE-
XENE AT 80°C, 95 BAR $CO/H_2 = 1$ ($[Co_2(CO)_8]_0 = 6.6 \times 10^{-3}$ mol l^{-1} in methylcyclohexane)

Parameter	1-Octene	Cyclohexene
Concentration in mol l^{-1}		
$[Co_2(CO)_8]$ [a]	4.4×10^{-3}	3.2×10^{-3}
$[HCo(CO)_4]$ [a]	1.3×10^{-3}	4.6×10^{-3}
[acyl] [a]	2.7×10^{-3}	$< 0.3 \times 10^{-3}$
[olefin]	0.83	1.15
$[H_2]$ [b]	0.25	0.25
[CO] [b]	0.5	0.5
Pseudo first order rate constants in min^{-1}		
k_1'	4.2×10^{-3}	
k_2'	0.53	2.2×10^{-2}
k_3'	0.25	> 0.29
Second order rate constants in l mol^{-1} min^{-1} at 48 bar CO partial pressure		
k_1	1.7×10^{-2}	
k_{-1}	0.1	
k_2	0.64	1.9×10^{-2}
k_3	1.0	> 1.2
k_4	5.1	> 8.0
Reaction rates in mol l^{-1} min^{-1}, at 48 bar CO partial pressure		
$r_1 = k_1[Co_2(CO)_8][H_2]$	1.8×10^{-5}	1.3×10^{-5}
$r_{-1} = k_{-1}[HCo(CO)_4]^2$	1.7×10^{-7}	2.1×10^{-6}
$r_2 = k_2[HCo(CO)_4][olefin]$	6.9×10^{-4}	9.9×10^{-5}
$r_3 = k_3[acyl][H_2]$	6.7×10^{-4}	8.8×10^{-5}
$r_4 = k_4[HCo(CO)_4][acyl]$	1.8×10^{-5}	1.1×10^{-5}
r_3/r_4	37	8
$r_{ald} = d[ald]/dt$	6.9×10^{-4}	9.9×10^{-5}

[a] Equilibrium concentration. [b] From ref. 8.

In the absence of olefin $Co_2(CO)_8$ is converted into $HCo(CO)_4$, until after ~ 24 h an equilibrium is reached in which 67% of the cobalt is present as $HCo(CO)_4$ and 33% as $Co_2(CO)_8$.

1-Octene

When 1-octene is added to this equilibrium mixture the $HCo(CO)_4$ concentration drops sharply to 10%. At the same time $Co_2(CO)_8$ (70%) and acylcobalt tetra-carbonyl (20%) are formed. The composition of this new steady state remains constant for several hours (Table 2).

The formation of the aldehydes starts as soon as the new steady state is reached. All possible isomers are formed with 1-nonanal (75%) as the major product. Only small amounts of other side products (< 2%) are formed.

After 24 h, when most of the octene has reacted, the acyl complex disappears and instead the concentrations of $HCo(CO)_4$, and to a lesser extent $Co_2(CO)_8$, increase (see Fig. 1). If the reaction is followed for a longer time the system tends to return to the original equilibrium situation observed in the absence of olefin. At this stage no other carbonyl containing species can be detected by IR and UV spectroscopy.
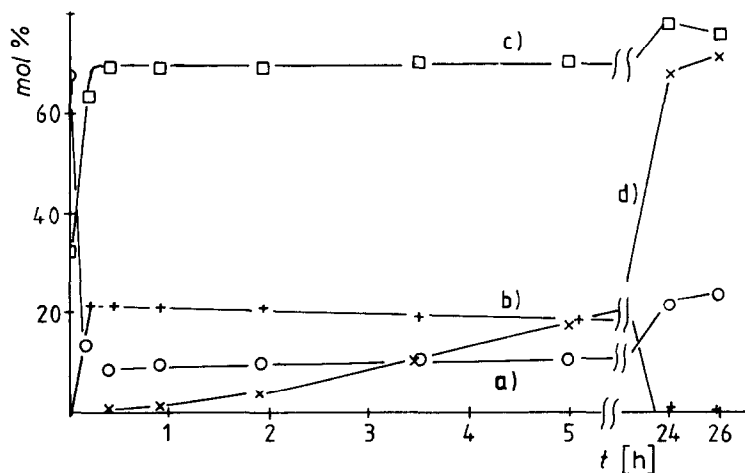
Fig. 1. Composition of the reaction mixture during the hydroformylation of 1-octene. (Conditions as in Table 2). % of Co as (a) $HCo(CO)_4$; (b) $RCOCo(CO)_4$; (c) $Co_2(CO)_8$; (d) aldehyde yield.

The decrease of the 1-octene concentration conforms to the first order rate law. The rate constant for the hydroformylation was found to be

$$k_{ald} = 0.83 \times 10^{-3} \text{ min}^{-1} \text{ (see Fig. 2).}$$

Cyclohexene

Cyclohexene shows a somewhat different behaviour. Within a few minutes after the addition of cyclohexene to an equilibrium mixture of $Co_2(CO)_8$ and $HCo(CO)_4$ the concentration of the $HCo(CO)_4$ decreases sharply and the concentration of $Co_2(CO)_8$ increases. Some 32% of the initial cobalt could not be accounted for. No
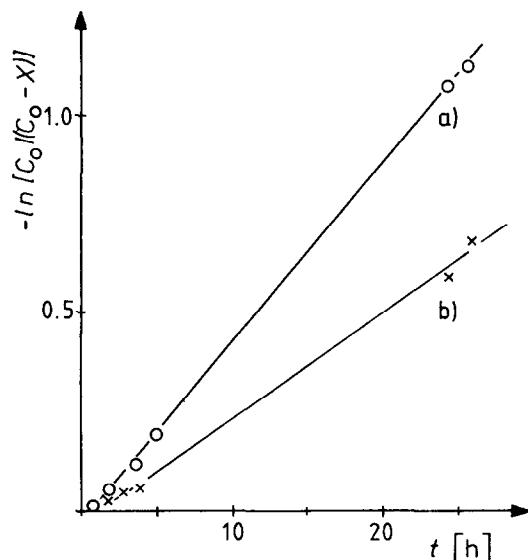

Fig. 2. Olefin conversion as a function of time; (a) 1-octene; (b) cyclohexene $\times$ 5.

other cobalt species can be detected by IR and UV spectroscopy, and no hydroformylation or hydrogenation takes place during these initial changes in the catalyst composition. During the next 2 h the concentration of $HCo(CO)_4$ increases and that of $Co_2(CO)_8$ decreases, until a new steady state concentration is reached with 42% of the cobalt as $HCo(CO)_4$ and 58% as $Co_2(CO)_8$ (see Table 2). Both carbonyls together account for 80% of the original cobalt content (see Fig. 3).

When the equilibrium is reached, the hydroformylation starts to yield cyclohexane aldehyde and a small amount of cyclohexane ($\sim$ 1%). These are the only detectable products. The rate constant for the hydroformylation is
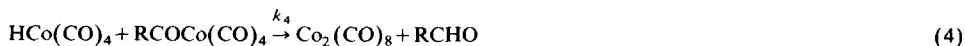
$$k_{ald} = 8.6 \times 10^{-5} \text{ min}^{-1}$$

Thus the reaction of cyclohexene is much slower than that of 1-octene (see Fig. 2).

No acylcobalt tetracarbonyl could be identified in the IR spectra during the cyclohexene hydroformylation. Taking account of the detection limit, the steady state concentration of acylcobalt tetracarbonyl must thus be $< 0.3 \times 10^{-3}$ mol l^{-1} (see Table 2).

Treatment of data

The more detailed mechanism of the hydroformylation, as proposed by Heck and Breslow [6] in Scheme 1, can be simplified to four essential steps (see Scheme 2):

$$H_2 + Co_2(CO) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2 HCo(CO) \tag{1}$$

$$HCo(CO)_4 + \text{olefin} + CO \overset{k_2}{\rightarrow} RCOCo(CO)_{44} \tag{2}$$

$$H_2 + RCOCo(CO)_4 \overset{k_3}{\rightarrow} HCo(CO)_4 + RCHO \tag{3}$$

$$HCo(CO)_4 + RCOCo(CO)_4 \overset{k_4}{\rightarrow} Co_2(CO)_8 + RCHO \tag{4}$$

$$-d[Co_2(CO)_8]/dt = 0 = k_1'[Co_2(CO)_8] - k_{-1}[HCo(CO)_4]^2 - k_4[HCo(CO)_4][\text{acyl}]$$

$$k_4 = \left(k_1'[Co_2(CO)_8] - k_{-1}[HCo(CO)_4]^2\right)/[HCo(CO)_4][\text{acyl}]$$

$$d[\text{acyl}]/dt = 0 = k_2'[HCo(CO)_4] - k_3'[\text{acyl}] - k_4[HCo(CO)_4][\text{acyl}]$$
$$= r_2 - r_3 - r_4$$

$$k_2' = \left(k_3'[\text{acyl}] + k_4[HCo(CO)_4][\text{acyl}]\right)/[HCo(CO)_4] = r_{ald}/[HCo(CO)_4]$$

$$r_{ald} = d[\text{ald}]/dt = k_3'[\text{acyl}] + k_4[HCo(CO)_4][\text{acyl}]$$

$$k_3' = r_{ald}/[\text{acyl}] - k_4[HCo(CO)_4]$$

$$r_{ald} = r_3 + r_4; \quad r_3 = r_{ald} - r_4$$

$$k_1' = k_1[H_2]; \quad k_2' = k_2[\text{olefin}]; \quad k_3' = k_3[H_2]$$

r = rate; k' = pseudo first order rate constant; k = second order rate constant

SCHEME 2. Simplified hydroformylation mechanism.

1. The formation of the cobalt carbonyl hydride from $Co_2(CO)_8$.
2. The activation of the olefin in a reaction with $HCo(CO)_4$ and the subsequent activation of carbon monoxide with formation of the acyl complex.
3. The reaction of the acyl complex with H_2 to complete the catalytic cycle, with formation of aldehyde and $HCo(CO)_4$.
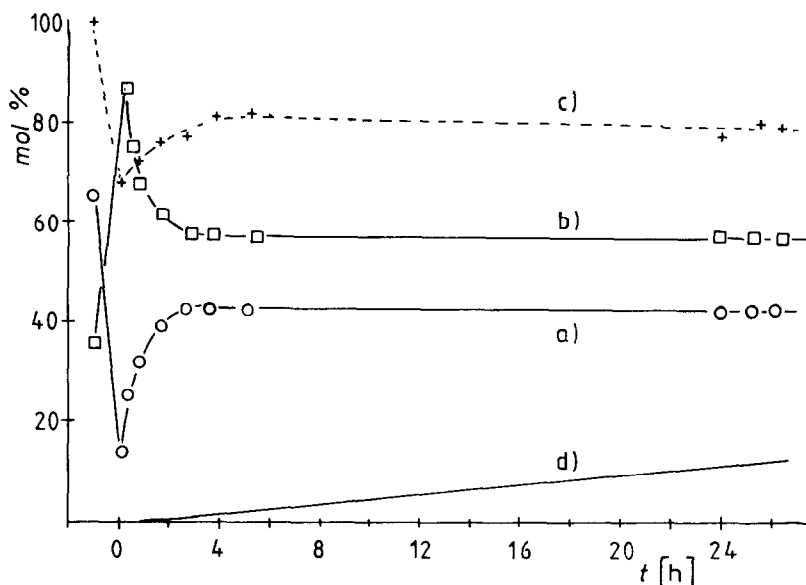
Fig. 3. Composition of the reaction mixture during the hydroformylation of cyclohexene. (Conditions as in Table 2). % of IR detectable Co as (a) $HCo(CO)_4$; (b) $Co_2(CO)_8$; (c) IR detectable Co-species in % of starting Co; (d) aldehyde yield.

4. The reaction of the acyl complex with $HCo(CO)_4$, to give $Co_2(CO)_8$ and the aldehyde.

The concentrations of the compounds in Scheme 2 are known, and therefore the rates and rate constants for the four steps can be calculated.

Since there is a large excess of H_2 and CO, on the assumption that the reverse reaction is second order in $HCo(CO)_4$, the simplified form $A \rightleftharpoons 2B$ can be applied for the kinetics of eq. 1 [22]. The rate constants k_1 and k_{-1} can then be determined in the absence of olefin. Since the concentrations of the cobalt species remain constant during the hydroformylation for extended periods of time, steady state kinetics can be applied. With the concentrations of H_2, CO, and olefin defined as constant, the reactions 2 and 3 become pseudo first order. The second order rate constants are obtained by division of the pseudo first order rate constants k' by the concentration of the appropriate species.

Discussion

The data from Table 2 give a quite clear picture of how the hydroformylations of 1-octene and cyclohexene proceed. Aldehydes are produced via two alternative routes (a) the reaction of $RCOCo(CO)_4$ with H_2 (cycle A in Scheme 1) and (b) its reaction with $HCo(CO)_4$ (cycle B in Scheme 1). However, the hydrogen route is strongly favoured by a factor of 37/1 for 1-octene and 8/1 for cyclohexene under the conditions of our experiment. The factor is expected to increase further when more severe conditions are applied since cycle A is determined by k_3 and $[H_2]$, and $[H_2]$ will increase with temperature and pressure, although the effect of the H_2 concentration may partially be compensated by an increasing CO partial pressure (vide infra). On the other hand cycle B is mainly limited by the concentration of

$HCo(CO)_4$, and this is not expected to increase very much under more severe conditions. Therefore we can conclude that under the conditions of the catalytic hydroformylation, cycle A via hydrogen is mainly responsible for the aldehyde formation. Recently published experiments performed with D_2 support this result [24].

The rate constant k_1 for the formation of $HCo(CO)_4$ from $Co_2(CO)_8$ is the smallest of all the measured rate constants. Therefore cycle B is better viewed as an exit from the catalytic cycle rather than an alternative product-forming step, since it interrupts the catalytic system. Whyman [7] suggests that k_2 is rate-determining for cyclohexene and $(k_3 + k_4)$ is rate-determining for 1-octene. In our experiments we found the rate constant is lowest for the reaction of the olefin with $HCo(CO)_4$ (k_2) for both olefins examined. For 1-octene k_3 is only slightly higher than k_2, and this ratio may be reversed at higher temperatures.

The experiments qualitatively confirm Whyman's results in so far as the reaction of cyclohexene with $HCo(CO)_4$ is much slower than that of 1-octene. This conclusion is supported by the calculated rates and rate constants, derived from our experiments. In addition, we have shown that the formation of $HCo(CO)_4$ is the slowest step in the catalytic cycle.

These results are not in agreement with Alemdaroglu's conclusion [8–10] that the aldehyde formation proceeds via a reaction of the acylcobalt tetracarbonyl with $HCo(CO)_4$, although our experimental results are qualitatively and quantitatively similar to his. The reason for the discrepancy is that Alemdaroglu does not compare the rates of the two alternative product-forming steps but only the rate constants. Thus he neglects the fact that under catalytic conditions the $HCo(CO)_4$ concentration is much lower than the H_2 concentration, and therefore $r_4 < r_3$. His statement: "...we have never observed with any olefin a hydroformylation reaction which is faster than the rate of formation of $HCo(CO)_4$ from $Co_2(CO)_8$..." is wrong and not in agreement with his own results (comp. also ref. 12). Unfortunately his product studies and his spectroscopic experiments were performed under different conditions. Therefore it is not possible to calculate absolute rates from his data, but it seems that the hydroformylation of 1-pentene is at least 100 times faster than the formation of $HCo(CO)_4$.

Under the conditions described in this paper, the formation of $HCo(CO)_4$ from $Co_2(CO)_8$ proceeds via an associative pathway, as was shown in a separate study [22]. The reverse reaction, namely the formation of $Co_2(CO)_8$ from $HCo(CO)_4$ is negligible as long as it is second order in $HCo(CO)_4$, since its stationary concentration is low.

The abnormally high $Co_2(CO)_8$ concentration immediately after the addition of cyclohexene to $HCo(CO)_4$ in the experiment depicted in Fig. 3, has been observed previously [26]. At present any explanation of this effect would be speculative.

During the actual hydroformylation the main source of $HCo(CO)_4$ is the reaction of the acylcobalt tetracarbonyl with hydrogen, since $r_3 > r_1$. Its main consumption is by the reaction with the olefin (k_2 and r_2 in Table 2).

The terminal olefin 1-octene reacts much faster with $HCo(CO)_4$ than the internal olefin cyclohexene:

$k_2(\text{octene})/k_2(\text{cyclohexene}) = 34$

$r_2(\text{octene})/r_2(\text{cyclohexene}) = 7$

The rate constants for the reactions of the acyl complex (k_3 and k_4) are higher for cyclohexene than for 1-octene, indicating that the branched acyl complexes are more reactive toward H_2 and $HCo(CO)_4$, in agreement with stoichiometric investigations. The earlier work is consistent with a dissociative route via $RCOCo(CO)_3$ [27].

In our experiments, minor amounts of the corresponding hydrocarbon were formed only in the case of cyclohexene. The hydrogenation probably arises from a prefered reaction of the alkylcobalt tetracarbonyl intermediate with H_2 instead of $HCo(CO)_4$, unless the rate constant of reaction 5b is much higher than that of 5a.

$$RCo(CO)_4 + H_2 \rightarrow RH + HCo(CO)_4 \qquad (5a)$$

$$RCo(CO)_4 + HCo(CO)_4 \rightarrow RH + Co_2(CO)_8 \qquad (5b)$$

Acknowledgement

References

1 B. Cornils in J. Falbe, (Ed.), New Syntheses with Carbon Monoxide, Springer-Verlag Berlin, (1980), p. 1 ff.
2 P. Pino, F. Piacenti and M. Bianchi in I. Wender and P. Pino (Eds.), Organic Syntheses via Metal Carbonyls, Vol. 2, Wiley, New York, (1977), p. 43 ff.
3 O. Roelen in The Oxo Process, FIAT Final Report No. 1000, U.S. Dept. Commerce, Washington D.C. (1947) p. 26.
4 H. Adkins and G. Krsek, J. Am. Chem. Soc., 70 (1948) 383.
5 L. Kirch and M. Orchin, J. Am. Chem. Soc., 81 (1959) 3597.
6 R.F. Heck and D.S. Breslow, Actes congr. intern. catalyse, 2^e, Paris (1960), p. 671 (C.A. 55 (1961) 24545; Chem. & Ind. [London] (1960) 467; J. Am. Chem. Soc., 83 (1961) 4024.
7 R. Whyman, J. Organomet. Chem., 66 (1974) C23; R. Whyman, ibid., 81 (1974) 97.
8 N.H. Alemdaroglu, Dissertation T.H. Enschede, The Netherlands (1974).
9 M. van Boven, N.H. Alemdaroglu and J.L.M. Penninger, Ind. Eng. Chem., Prod. Res. Dev., 14 (1975) 259.
10 N.H. Alemdaroglu, J.M.L. Penninger and E. Oltay, Monat. Chem., 107 (1976) 1153.
11 N. Niwa and M. Yamaguchi, Shokubai, 3 (1961) 264.
12 R. Iwanaga, Bull. Chem. Soc. Jap., 35 (1962) 778.
13 M. Orchin and W. Rupilius, Catal. Rev., 6 (1972) 85.
14 M. Bianchi, F. Piacenti, P. Frediani and U. Matteoli, J. Organomet. Chem., 135 (1977) 387.
15 E. Debie, Dissertation RWTH Aachen (West Germany) 1978.
16 J.R. Norton, Acc. Chem. Res., 12 (1979) 139.
17 W.D. Jones, J.M. Huggins and R.G. Bergman, J. Am. Chem. Soc., 103 (1981) 4415.
18 T.E. Nalesnik and M. Orchin, Organometallics, 1 (1982) 223.
19 F. Ungváry and L. Markó, J. Organomet. Chem., 249 (1983) 411.
20 M.J. Mirbach, M.F. Mirbach, A. Saus, N. Topalsavoglu and T.N. Phu, J. Am. Chem. Soc., 103 (1981) 7590.
21 M.F. Mirbach, M.J. Mirbach, A. Saus and S. Schwerdt, Chemiker-Ztg., 106 (1982) 335.
22 M.F. Mirbach, to be published.
23 P. Szabo, L. Markó and G. Bor, Chem. Technol., 13 (1961) 549.
24 P. Pino, F. Oldani and G. Consiglio, J. Organomet. Chem., 250 (1983) 491.
25 K. Noack, Helv. Chim. Acta, 45 (1962) 1847.
26 R. Tannenbaum, Dissertation Nr. 6970, ETH Zürich (Switzerland) 1982.
27 R.F. Heck, J. Am. Chem. Soc., 85 (1963) 651.