Journal of Organometallic Chemistry, 66 (1974) C23—C25.

Preliminary communication

IN SITU INFRARED SPECTRAL STUDIES ON THE COBALT CARBONYL-CATALYSED HYDROFORMYLATION OF OLEFINS

R. WHYMAN

*Imperial Chemical Industries Ltd., Corporate Laboratory, P.O. Box 11,
The Heath, Runcorn, Cheshire (Great Britain)*

(Received August 17th, 1973)

Summary

High pressure infrared spectral studies suggest that the species predominating during the steady-state hydroformylation of olefins can be either acylcobalt tetracarbonyls or hydrido carbonyls, depending upon the nature of the olefin and the catalyst system.

Although the combination of kinetic measurements and studies of stoichiometric reactions under ambient conditions have produced a generally agreed picture concerning the mechanism of the cobalt carbonyl-catalysed hydroformylation of olefins [1] there is currently little direct evidence to show that the proposed intermediate species do in fact exist in solution under the high pressures (ca. 250 atm. CO/H_2 total pressure) and temperatures (ca. 150°) normally used. This communication describes our efforts to confirm some of the proposed mechanistic details by the direct observation of hydroformylation and related reactions in a high pressure infrared spectrophotometric cell [2].

Initially the basic reactions of both the liganded and non-liganded cobalt carbonyls were studied in the absence of olefin under the optimum pressures and temperatures reported for hydroformylation activity [$Co_2(CO)_8$ in heptane, 250 atm. CO/H_2, 150°, and $Co_2(CO)_6(PBu_3)_2$, 2 PBu_3, 80 atm. CO/H_2, 190° respectively] in order to demonstrate whether the proposed hydrido species $HCo(CO)_3L$, where L = CO or $P(n\text{-}Bu)_3$, are formed under these reaction conditions.

In both examples spectral changes in the 2200—1600 cm^{-1} region are consistent with equilibrium 1 being displaced well to the right hand side.

$$Co_2(CO)_6L_2 + H_2 \rightleftarrows 2HCo(CO)_3L \qquad (L = CO, PBu_3) \qquad (1)$$

Thus in the $Co_2(CO)_8$ system the high pressure-high temperature spectrum

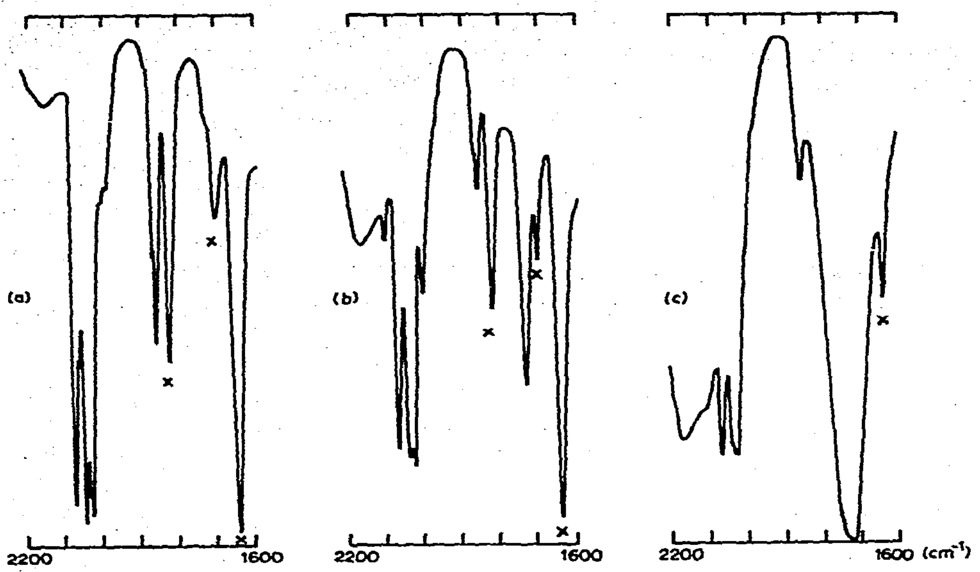

Fig. 1. Hydroformylation of 1-octene in the presence of $Co_2(CO)_8$ as catalyst precursor: (a) 250 atm. total pressure CO/H_2 (1/1) at 31°; (b) 280 atm. at 150°; (c) 200 atm. at 150°. Peaks identified by crosses are 1-octene absorptions.

shows absorptions at 2114 w, 2052 m, 2030 vs and 1993 vw cm^{-1}, consistent with the known solution spectrum of $HCo(CO)_4$ [3], the observation of an additional shoulder at 2068 cm^{-1} and a weak peak at 1858 cm^{-1} indicating the presence of a small amount of unchanged $Co_2(CO)_8$. Similarly, in the liganded system, the peaks at 1972 m(sh), 1953 vs, and 1927 w(sh) cm^{-1}, corresponding with the starting $[Co(CO)_3PBu_3]_2$, decrease in intensity and are replaced at high temperatures (above 160°) by bands at 2049 mw, 1970 vs, and 1935 w cm^{-1}, consistent with the spectrum of $HCo(CO)_3PBu_3$ [4]. Thus most of the $[Co(CO)_3PBu_3]_2$ is converted into the monosubstituted hydrido species under these conditions; the appearance of an additional peak at 1904 cm^{-1} suggests that a small amount of $HCo(CO)_2(PBu_3)_2$ [5] may be formed.

Spectra obtained during the hydroformylation of 1-octene catalysed by $Co_2(CO)_8$ at 250 atm. pressure CO/H_2 and 150° are illustrated in Fig. 1. Spectrum (a) corresponds with the normal room temperature solution spectrum of $Co_2(CO)_8$ and 1-octene and spectrum (b), measured in the early stages of the hydroformylation is very similar to that reported by Markó and coworkers [3] from sampling the contents of a hydroformylation mixture. This is the "steady-state" spectrum observed throughout the hydroformylation and is consistent with the presence of a mixture of $RCOCo(CO)_4$, where $R = C_8H_{17}$, and $Co_2(CO)_8$ (distinctive absorptions due to the acylcarbonyl species occur at 2103 and 2002 cm^{-1}). At the end of the hydroformylation, the spectrum, (c) may be interpreted in terms of the presence of a mixture of $HCo(CO)_4$ and $Co_2(CO)_8$, although the band widths are increased by the presence of large quantities of aldehyde.

On variation of the CO/H_2 ratio, with the total pressure and other variables kept constant, the amount of acyl species present in the steady-state spectrum is found to increase with increasing partial pressure of carbon monoxide, i.e. in the CO/H_2 order 3/1 > 1/1 > 1/3. This suggests that for the hydroformylation of 1-octene in the presence of $Co_2(CO)_8$ as catalyst precursor, hydrogenolysis of the acyl cobalt carbonyl is a rate-determining step.

Similar spectra are observed when 1-octene is replaced by ethylene but, in contrast, when an internal olefin such as diisobutylene or cyclohexene (which react more slowly than terminal olefins) is used, only $HCo(CO)_4$ and $Co_2(CO)_8$ are observed throughout the hydroformylation.

In the case of the liganded system (PBu_3/Co = 2/1) $HCo(CO)_3PBu_3$ predominates throughout the hydroformylation, together with smaller amounts of $Co_2(CO)_6(PBu_3)_2$. We have been unable to obtain any spectral evidence for the presence of an acyl species of the type $RCOCo(CO)_3PBu_3$ during the hydroformylation, irrespective of the nature of the olefin.

These results suggest that hydrogenolysis of the acyl species $RCOCo(CO)_4$ is only a significant rate-determining step in the fastest reactions, i.e. hydroformylation of simple terminal olefins catalysed by $Co_2(CO)_8$. In the slower reactions, i.e. hydroformylation of internal olefins in the presence of $Co_2(CO)_8$ or reactions involving the $Co_2(CO)_8$/PBu_3 catalyst system, initial interaction of the olefin with the hydrido species $HCo(CO)_3L$, where L = CO or PBu_3, appears to be the rate-determining step. This conclusion is consistent with recently reported kinetic studies on the hydroformylation of propylene catalysed by the $Co_2(CO)_8$/PBu_3 system [6].

References

1 J. Falbe, "Carbon Monoxide in Organic Synthesis", Springer-Verlag, Berlin, 1970, and references therein.
2 W. Rigby, R. Whyman and K. Wilding, J. Phys. E. Sci. Instrum., 3 (1970) 572.
3 L. Markó, G. Bor, G. Almázy and P. Szabó, Brennst.-Chem., 44 (1963) 184.
4 F. Piacenti, M. Bianchi and E. Benedetti, Chim. Ind. (Milan), 49 (1967) 245.
5 G.F. Pregaglia, A. Andreetta, G.F. Ferrari and R. Ugo, J. Organometal. Chem., 30 (1971) 387.
6 G.F. Pregaglia, A. Andreetta, G. Gregorio, G. Montrasi and G.F. Ferrari, Chim. Ind. (Milan), 54 (1972) 405.