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THE HYDROFORMYLATION OF OLEFINS CATALYSED BY COBALT CARBONYLS: A HIGH PRESSURE INFRARED SPECTRAL STUDY

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Summary

The hydroformylation of various olefins, e.g. 1-octene, ethylene, diisobutylene and cyclohexene, in the presence of $Co_2(CO)_8$ and $Co_2(CO)_8/P\text{-}n\text{-}Bu_3$ as catalyst precursors has been studied by following infrared spectral changes under optimum reaction conditions in a high pressure spectrophotometric cell. The results are basically consistent with the Heck mechanism for hydroformylation but significant differences in the rate-controlling steps have been observed. These suggest that hydrogenolysis of the acyl species $RCOCo(CO)_4$ is only a significant rate-determining step in reactions with the fastest rates, i.e. hydroformylation of simple terminal olefins catalysed by $Co_2(CO)_8$. In reactions with slower rates, e.g. hydroformylation of internal olefins or use of 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 $P\text{-}n\text{-}Bu_3$, appears to be the rate-determining step.

Introduction

Hydroformylation is the name used to describe the reaction of an olefin with carbon monoxide and hydrogen to yield an aldehyde:

$$RCH{=}CH_2 + CO + H_2 \rightarrow RCH_2CH_2CHO + RCH(CHO)CH_3$$

The reaction was discovered in 1938 by Roelen and was found to take place at high pressures and temperatures and to be catalysed by Group VIII metal carbonyls, particularly those of Co, Rh and Ir [1].

Because of the industrial importance of the hydroformylation reaction in the synthesis of plasticiser alcohols much effort has been devoted to an understanding of the mechanism of the reaction. The general reaction scheme, proposed by Wender, Sternberg, Orchin and Heck and co-workers for the cobalt carbonyl-catalysed reaction affording the straight chain isomeric aldehyde is as follows:

$$Co_2(CO)_6L_2 + H_2 \rightleftharpoons 2HCo(CO)_3L \rightleftharpoons 2HCo(CO)_2L + 2CO \quad (1)$$

$$HCo(CO)_xL + RCH{=}CH_2 \rightleftharpoons RCH_2CH_2Co(CO)_xL \quad (2)$$

$$RCH_2CH_2Co(CO)_xL + CO \rightleftharpoons RCH_2CH_2COCo(CO)_xL \quad (3)$$

$$RCH_2CH_2COCo(CO)_xL + H_2 \rightarrow RCH_2CH_2CHO + HCo(CO)_xL \quad (4)$$

(L = CO or PR_3, x = 2 or 3)

These reactions may be considered as (1) activation of catalyst by conversion of the parent carbonyl into a hydridocarbonyl species which is itself in equilibrium with coordinatively unsaturated hydridocarbonyl and carbon monoxide, (2) a formal insertion of the olefin into the Co—H bond of the hydridocarbonyl equilibrium mixture to give an alkylcobalt carbonyl, (3) a formal insertion of carbon monoxide into the Co—C bond of the alkyl to give the corresponding mixture of acylcobalt carbonyls and (4) hydrogenolysis of the acyl species to give an aldehyde with the regeneration of the catalyst.

In the case of $Co_2(CO)_8$ as catalyst precursor these individual reaction steps have been shown to occur, but generally in stoichiometric reactions under conditions which are far removed from normal operating conditions, and there is little direct evidence to show that the proposed intermediate species do in fact exist in solution under the high pressures (250 atm CO/H_2) and temperatures (150°C) commercially used in hydroformylation.

In previous work we have studied the basic reactions of cobalt, rhodium and iridium carbonyls and their phosphine-substituted derivatives with high pressures of carbon monoxide and hydrogen [2]. Infrared spectral evidence has been obtained for the cleavage of dinuclear and tetranuclear species with the formation of hydridocarbonyls of the type $HM(CO)_3L$, where L = CO or PR_3 and M = Co, Rh and Ir, i.e. step (1) in the above reaction sequence. In several cases evidence for the formation of $HM(CO)_3L$ was only obtained under the high CO/H_2 pressures and temperatures similar to those used in hydroformylation, and reversion to the starting material occurred on cooling or on releasing the excess pressure.

In order to investigate the contribution of other reaction steps to the proposed hydroformylation sequence we have studied the reactions of the common cobalt catalyst precursors, i e. $Co_2(CO)_8$ and $Co_2(CO)_8$/P-n-Bu_3 in the presence of both terminal and internal olefins under their respective optimum hydroformylation conditions and the results obtained are described in this paper. Preliminary accounts of this work have appeared previously [3].

Results

Examples of the spectra which have been obtained during the hydroformylation reactions are shown in Figs. 1—4. The reactions were initially studied in the absence of olefin in order to determine the extent of conversion of metal carbonyl into hydridocarbonyl under optimum hydroformylation conditions. Thus Fig. 1 illustrates the spectra obtained when heptane solutions of $Co_2(CO)_8$ (0.2% Co by wt.) are pressurised with CO/H_2 (250 atm, 1/1 gas ratio) and heated

(continued on p 102)

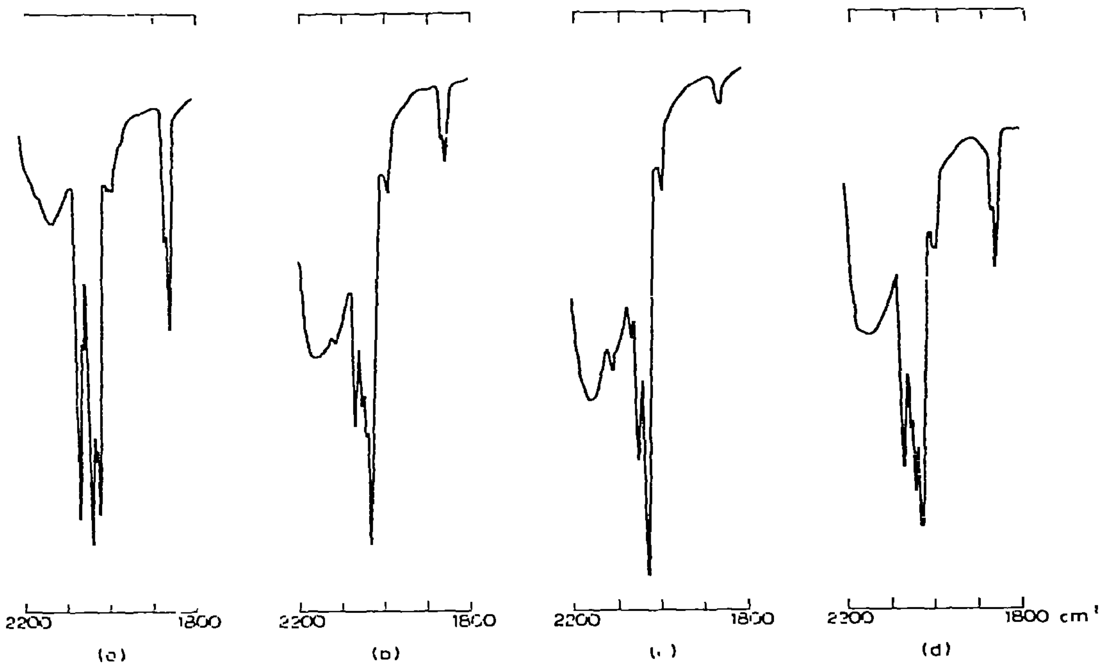

Fig 1 Reaction of $Co_2(CO)_8$ with CO/H_2 (1/1) in heptane (a) 270 atm total pressure at 30°, (b) 290 atm at 120°, (c) 290 atm at 150° (d) 250 atm at 20°

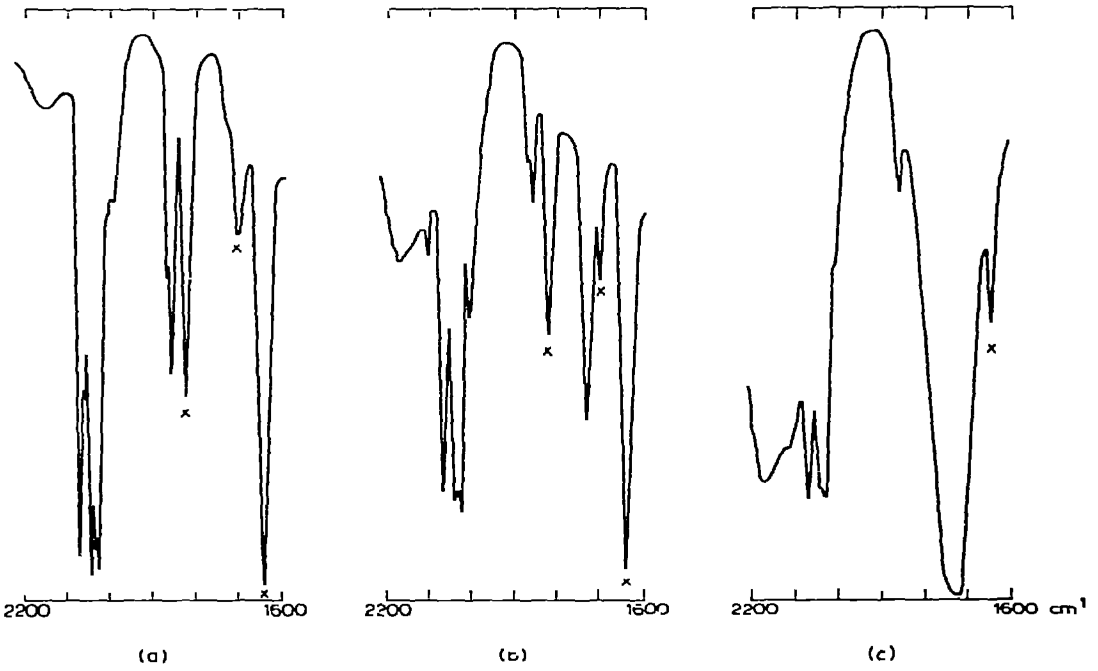

Fig 2 Hydroformylation of 1-octene in the presence of $Co_2(CO)_8$ as catalyst precursor (a) 250 atm total pressure CO/H_2 (1/1) at 31°, (b) 280 atm at 150°C, (c) 200 atm at 150° Peaks identified by crosses are 1-octene absorptions

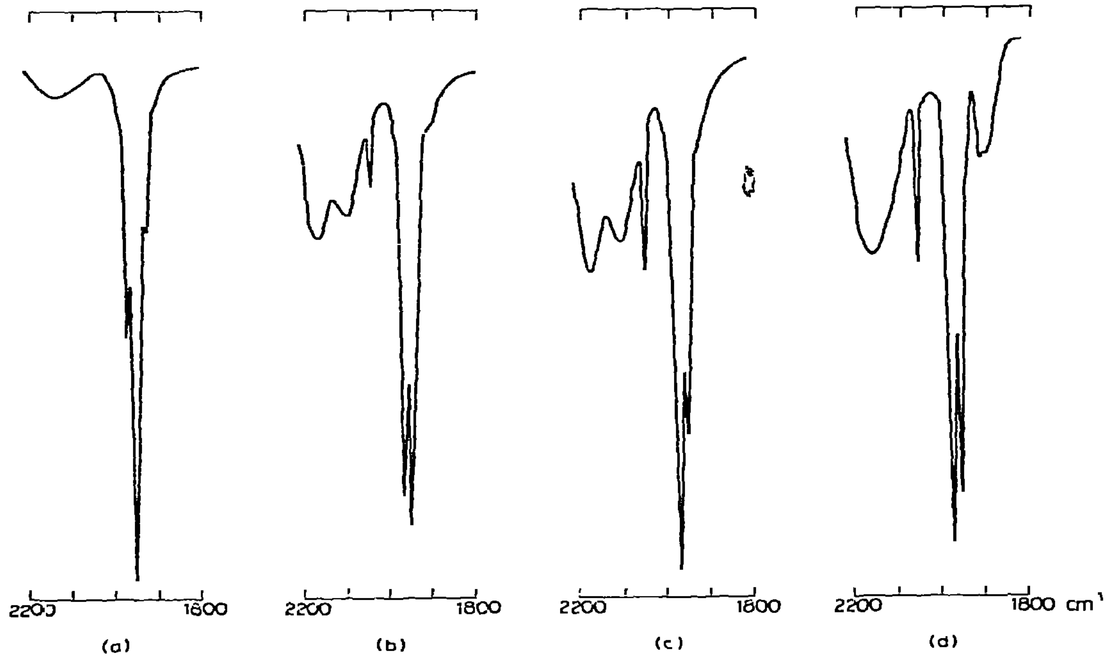

Fig 3 Reaction of $[Co(CO)_3PBu_3]_2$ $2PBu_3$ with CO/H_2 (1/1) in heptane (a) 70 atm total pressure at 50 (b) 80 atm at 170°, (c) 80 atm at 190°, (d) 70 atm at 50°

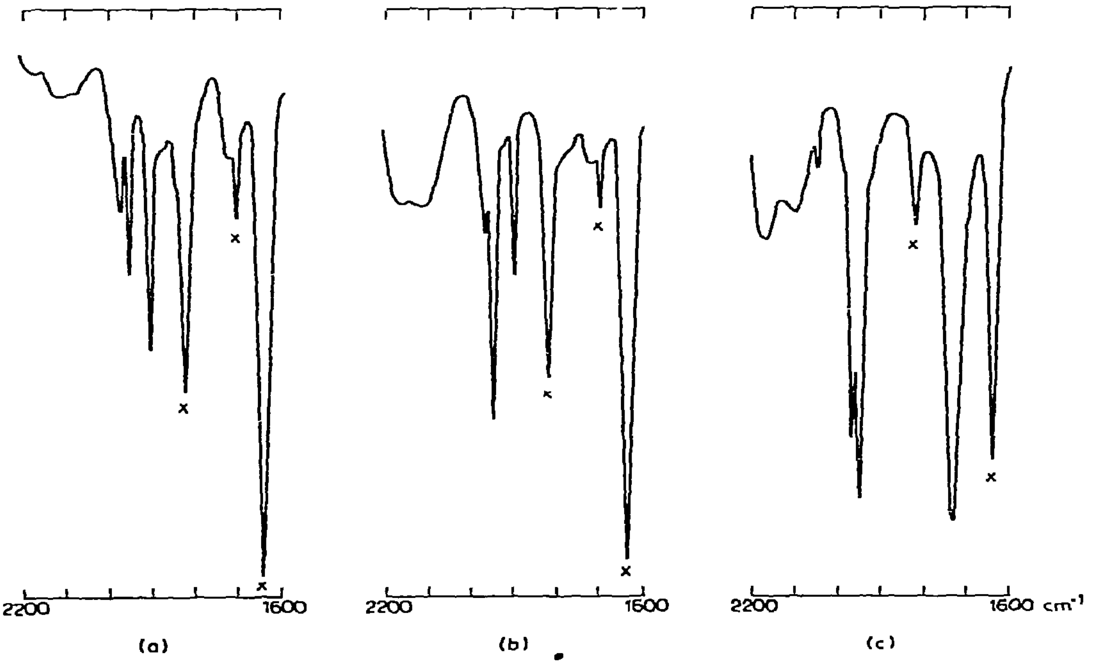

Fig. 4 Hydroformylation of 1-octene in the presence of $Co_2(CO)_8$ and $4PBu_3$ as catalyst precursor. (a) 70 atm total pressure CO/H_2 (1/1) at 25°. (b) 79 atm at 170°; (c) 75 atm at 190° Peaks identified by crosses are 1-octene absorptions.

TABLE 1

METAL CARBONYL STRETCHING FREQUENCIES (cm^{-1})

Fig 1c	$Co_2(CO)_8$	$HCo(CO)_4$[a]
2114 w		2114 w
2068 w	2070 s	
	2059 (sh)	
2052 ms		2052 m
	2044 s(sh)	
	2042 s	
2030 s	2031 m(sh)	2030 s
	2022 s	
	2002 vw	
1993 w		1993 vw
	1866 mw(sh)	
1858 w	1857 m	

[a] From ref 5

TABLE 2

METAL CARBONYL STRETCHING FREQUENCIES (cm^{-1})

Fig 2b	$Co_2(CO)_8$	$HCo(CO)_4$	$CH_3Co(CO)_4$[a]	n $C_8H_{17}COCo(CO)_4$[a]
		2114 w		
2103 w			2105 w	2103 m
2068 s	2070 s			
	2059 (sh)			
	2044 s(sh)	2052 m		
2041 s	2042 s			2044 s
2030 (sh)	2031 m(sh)	2030 s	2036 m	
2022 s	2022 s		2019 vs	2022 s
2002 m	2002 vw	1993 vw		2003 vs
	1866 mw(sh)			
1858 mw	1857 m			
				1720 m

[a] From ref 8

TABLE 3

METAL CARBONYL STRETCHING FREQUENCIES (cm^{-1})

Fig 3c	$Co_2(CO)_6L_2$[a]	$Co_2(CO)_7L$[a]	$HCo(CO)_3L$[a]	$HCo(CO)_2L_2$[a] [b]
		2081 m		
2049 mw			2049 mw	
		2024 m		
		1994 s		
1970 vs	1972 w		1970 vs	1977 ms
1953 ms	1953 vs	1955 mw		1958 s
			1935 vw	1942 w
	1927 vw(sh)			1912 (sh)
1904 vw(sh)				1902 vs

[a] L = PBu_3 [b] From ref 10

to 150°C. Fig. 2 shows the spectra obtained from the same reaction in the presence of 1-octene (1-octene/heptane 3/1). Similarly Figs. 3 and 4 illustrate the spectra obtained from the corresponding reactions in the presence of tri-n-butylphosphine (0.1—0.2% Co by wt., PBu_3/Co 2/1, 80 atm CO/H_2 (1/1), 190°C). Tables 1—3 summarise the accurate band maxima noted in the different experiments during steady-state hydroformylation conditions, together with the spectra of related species for comparison

Discussion

Hydroformylation with $Co_2(CO)_8$ as catalyst precursor

Comparison of the absorption maxima in Fig. 1c with the known spectra of $Co_2(CO)_8$ [4] and $HCo(CO)_4$ [5] (see Table 1) clearly indicates the predominance of the latter species at 290 atm pressure and 150°C. The appearance of weak peaks at 2068 and 1858 cm^{-1} suggest that a small amount of $Co_2(CO)_8$ remains unchanged and on cooling to room temperature (Fig. 1d) partial reconversion into $Co_2(CO)_8$ occurs Clearly, however, the equilibrium

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4$$

lies well over on the right hand side at 290 atm pressure and 150°C. It is relevant to note that under the high pressure-high temperature conditions there are no additional absorptions which could be attributed to the presence of a species such as $HCo(CO)_3$ [6]; the concentration of this species has been estimated to be $< 1\%$ of the $HCo(CO)_4$ concentration under hydroformylation conditions. Also, there is no evidence for the formation of $Co_2(CO)_9$ [7]. In Fig. 2 (the peaks marked with crosses are due to olefin absorptions) the initial spectrum is again consistent with the normal solution spectrum of $Co_2(CO)_8$ and the only change noted on heating to 120°C is a decrease in the intensity of the bridging carbonyl frequencies. This may well be due to the stabilisation of the non-bridged isomer of $Co_2(CO)_8$ at these higher temperatures. Marked spectral changes are observed at 150°C on commencement of hydroformylation (as indicated by the appearance and rapid increase in intensity of a band at 1730 cm^{-1} due to aldehyde formation). In the terminal carbonyl region new bands are observed at 2103 and 2002 cm^{-1} and the relative intensities of the bands at ca. 2020 cm^{-1} are altered. This spectrum (Fig. 2b) is in fact the "steady-state" spectrum and only towards the end of the hydroformylation are further changes noted. At this stage (Fig. 2c) the bands are broadened by the solvent effect of the large concentration of aldehyde but the spectrum may be interpreted in terms of the presence of both $HCo(CO)_4$ and $Co_2(CO)_8$.

Comparison of the band maxima in Fig. 2b with the spectra of $HCo(CO)_4$ and $CH_3Co(CO)_4$ (see Table 2) immediately eliminates the presence of hydrido- and alkyl-cobalt tetracarbonyls during the hydroformylation. The steady-state spectrum is most consistent with the presence of a mixture of $RCOCo(CO)_4$ and $Co_2(CO)_8$ and is in fact very similar to that obtained by Markó and co-workers from sampling the contents of a hydroformylation reaction mixture [8].

This hydroformylation has also been studied at carbon monoxide to hydrogen ratios of 3/1 and 1/3, while maintaining the cobalt and olefin concentrations and the total pressure constant. The spectra obtained show that the amount of acyl species present in the steady-state hydroformylation mixture increases with increasing partial pressure of carbon monoxide, i.e. in the CO/H_2 order 3/1 > 1/1 > 1/3. These results indicate that for the hydroformylation of 1-octene in the presence of $Co_2(CO)_8$ as catalyst precursor, hydrogenolysis of the acyl species (step 4 in the reaction sequence) is a rate-determining step in the reaction.

If ethylene (40 atm) is substituted for 1-octene the spectra obtained during hydroformylation are very similar, showing additional bands at 2105 and 2003 cm^{-1}, this time consistent with the presence of a mixture of $C_2H_5COCo(CO)_4$ [8] and $Co_2(CO)_8$ This implies the operation of a similar rate-determining step throughout the hydroformylation of the terminal olefin series. However, when the hydroformylation of internal olefins (which are known to react more slowly than their terminal isomers) is studied, significant differences in the steady-state spectra have been observed. Thus spectra obtained during the hydroformylation of diisobutylene or cyclohexene are consistent with the presence of $HCo(CO)_4$ and $Co_2(CO)_8$ only throughout the reaction. There is no spectral evidence for the presence of significant amounts of the acylcobalt tetracarbonyls. This suggests that a different rate-determining step operates during the hydroformylation of internal olefins and this is probably the initial interaction of the olefin with $HCo(CO)_4$ (step 2 in the reaction sequence)

Hydroformylation with $Co_2(CO)_8$/P-n-Bu_3 as catalyst precursor

The utilisation of phosphines as modifiers to the conventional cobalt carbonyl-catalysed hydroformylation reaction has recently been described [1] and their addition produces the following effects· (i) the reaction rate is lowered, (ii) the isomer distribution is altered to favour straight rather than branched chain products and (iii) under similar reaction conditions to the non-liganded process the products tend to be alcohols rather than aldehydes Linked with the last point is the fact that hydrogenation of the starting olefin to corresponding alkane becomes a significant side reaction.

As with the non-liganded cobalt carbonyl system we have studied the reaction under optimum hydroformylation conditions both with and without added olefin. In order to obtain the desired P/Co ratio we have used a variety of starting systems, e g. $Co_2(CO)_6(PBu_3)_2$ + $2PBu_3$, $Co_2(CO)_8$ + $4PBu_3$ and $Co_4(CO)_{12}$ + $8PBu_3$, and although the initial components are different the high pressure, high temperature spectra are all virtually identical.

Comparison of the band maxima in Fig. 3c with the spectra of the starting $Co_2(CO)_6(PBu_3)_2$ and $HCo(CO)_3PBu_3$ [9] (see Table 3) again indicates that the hydrido species predominates under optimum hydroformylation conditions although the equilibrium 1 lies further to the left than when L = CO. The appearance of a weak shoulder at 1904 cm^{-1} suggests that possibly a very small amount of $HCo(CO)_2(PBu_3)_2$ is present in the reaction mixture [10]. On cooling to room temperature while still under pressure (Fig 3d), partial reconversion of $HCo(CO)_3PBu_3$ into $Co_2(CO)_6(PBu_3)_2$ occurs; releasing the excess pressure causes complete reversion to the starting material.

If the reaction of $Co_2(CO)_6(PBu_3)_2$ with CO/H_2 is studied in the absence of excess phosphine, e g. a cobalt to phosphorus ratio of 1/1, then $Co_2(CO)_7PBu_3$ is also observed in the reaction mixture at 90 atm and 190°C. At higher pressures, e.g 300 atm, evidence for further reaction with the formation of $HCo(CO)_4$ has been obtained. Thus the function of the excess phosphine appears to be simply to inhibit the dissociation of the ligand, i e. maintaining the following equilibria on the left hand side.

$$Co_2(CO)_6L_2 + CO = Co_2(CO)_7L + L$$

$$HCo(CO)_3L + CO = HCo(CO)_4 + L$$

Fig. 4a is consistent with the spectrum of $HCo(CO)_2(PBu_3)_2$, together with absorptions due to 1-octene (identified by crosses) On addition of tri-n-butylphosphine to $Co_2(CO)_8$ the bulk of the initial product is known to be $[Co(CO)_3(PBu_3)_2][Co(CO)_4]$, which separates as an insoluble precipitate at room temperature and hence is not seen initially in the spectra. At 170°C (Fig. 4b) the band at 1950 cm^{-1} has increased considerably in intensity, suggesting that both $HCo(CO)_2(PBu_3)_2$ and $[Co(CO)_3(PBu_3)_2][Co(CO)_4]$ are being converted into $Co_2(CO)_6(PBu_3)_2$ At 190°C (Fig. 4c) new bands consistent with the formation of $HCo(CO)_3PBu_3$ are observed and hydroformylation commences, as evidenced by the appearance of the aldehyde absorption at 1730 cm^{-1} This spectrum remains virtually unchanged throughout the hydroformylation although the concentration of $HCo(CO)_3PBu_3$ increases very slightly with time There is no evidence for the presence of the known alkyl or acyl species of the types $RCo(CO)_3PBu_3$ or $RCOCo(CO)_3PBu_3$ [9] and this suggests the operation of a different rate-controlling step from that observed with the corresponding $Co_2(CO)_8$-catalysed hydroformylation of terminal olefins. This result suggests that initial interaction of the olefin with $HCo(CO)_3PBu_3$ is the critical factor, a feature which is also supported by the increased tendency for hydrogenation of the olefin using this system. If the bulk of the catalyst was in the form of $RCOCo(CO)_3PBu_3$ then presumably hydrogenation of olefin to alkane would be minimised.

If the hydroformylation of 1-octene catalysed by this system is studied at a 3/1 ratio of CO/H_2, keeping all other variables constant, then additional bands are observed in the spectra at 190°C. These occur at 2081, 2024 and 1994 cm^{-1} and are consistent with the presence of $Co_2(CO)_7PBu_3$, the higher partial pressure of carbon monoxide having resulted in some dissociation of the ligand. Again however no bands which are attributable to species such as $RCo(CO)_3$-PBu_3 or $RCOCo(CO)_3PBu_3$ are observed. A similar effect occurs when a P/Co ratio of 1/1 is employed.

When the hydroformylation of internal olefins, e g. diisobutylene and cyclohexene, is studied under the standard conditions, reaction takes place very slowly but the spectra observed are very similar to those obtained with 1-octene, suggesting the presence of only $HCo(CO)_3PBu_3$ and $Co_2(CO)_6(PBu_3)_2$ during the reaction. These results suggest that initial interaction of the olefin with the hydrido species $HCo(CO)_3PBu_3$ is the rate-controlling step irrespective of the nature of the olefin when the $Co_2(CO)_8/PBu_3$ catalyst system is employed.

In conclusion therefore the results obtained with $Co_2(CO)_8$ and $Co_2(CO)_8/PBu_3$ as catalyst precursors are consistent with the generally accepted mechanism for hydroformylation [1] although there appear to be significant differences in the rate-determining steps for different olefins and catalyst systems. Thus, hydrogenolysis of the acyl species $RCOCo(CO)_4$ is a significant rate-determining step only in reactions with the fastest rates, i.e. hydroformylation of simple terminal olefins catalysed by $Co_2(CO)_8$. In reactions with slower rates, e.g. hydroformylation of internal olefins or use of 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

The conclusions concerning different rate-determining steps are supported by results obtained from recent kinetic studies on the $Co_2(CO)_8/PBu_3$ catalyst system [11]. Here, although the kinetics is not first order on total cobalt concentration, comparison of the rate of hydroformylation of propylene with the estimated concentration of $HCo(CO)_3PBu_3$ (obtained from measurements of the equilibrium constant for the reaction $Co_2(CO)_6(PBu_3)_2 + H_2 \rightleftharpoons 2HCo(CO)_3PBu_3$) shows a direct proportionality, i e. rate = $k[HCo(CO)_3PBu_3]$, where k includes a kinetic constant and concentrations of olefin, hydrogen, and carbon monoxide

Unfortunately the comparison cannot be extended to the non-liganded cobalt carbonyl catalyst system because kinetically this reaction is extremely complex and a particular rate equation may strictly apply only over a limited range of reaction conditions [12].

Experimental

Spectral measurements under pressure

The design, construction and mode of operation of the high pressure infrared cell has been described previously [13]. Infrared spectra were recorded with a Perkin—Elmer Model 257 spectrophotometer using X10 scale expansion and calibration with either gaseous carbon monoxide or water vapour.

Preparation of catalyst precursors

The complexes $Co_2(CO)_8$ and $Co_2(CO)_6(PBu_3)_2$ were prepared by established methods [14,15] Tri-n-butylphosphine was obtained from Aldrich Chemical Company and used without further purification

Purification of olefins

Ethylene was dried by passing through 3A molecular sieve —BTS— 3A molecular sieve columns. 1-Octene (BDH Chemicals Ltd), cyclohexene (BDH Chemicals Ltd.) and diisobutylene (Ralph N Emanuel Ltd , mixture of 2,4,4-trimethyl-1-pentene (75%) and 2,4,4-trimethyl-2-pentene (25%)) were generally distilled immediately before use. Slight variations in reaction rate were noted depending on whether or not the olefin had been freshly distilled, there were however no significant differences between corresponding spectra

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