Journal of Organometallic Chemistry, 84 (1975) 65—74
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IN SITU IR SPECTROSCOPIC STUDIES OF THE COBALT CARBONYL/ TRI-n-BUTYLPHOSPHINE HYDROFORMYLATION CATALYST. II*

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(Received May 20th, 1974)

Summary

The reaction between dicobalt octacarbonyl and tri-n-butylphosphine in heptane was studied in the following range of reaction conditions: temperature 100-150°C, partial pressures of hydrogen and carbon monoxide 11-74.5 atm and 3-54 atm respectively, and phosphorus-to-cobalt ratios from zero to 13.7. The concentration of $Co_2(CO)_8$ was held constant at around 2 mmol l^{-1}. The carbonyl species present were analysed in situ by means of high temperature—pressure IR spectroscopy; they were found to be controlled by the following equilibria:

$$Co_2(CO)_8 \rightleftharpoons 2HCo(CO)_4 \qquad (1)$$

$$Co_2(CO)_8 + PBu_3 \rightleftharpoons Co_2(CO)_7PBu_3 + CO \qquad (2)$$

$$Co_2(CO)_7PBu_3 + H_2 \rightleftharpoons HCo(CO)_4 + HCo(CO)_3PBu_3 \qquad (3)$$

$$HCo(CO)_4 + PBu_3 \rightleftharpoons HCo(CO)_3PBu_3 + CO \qquad (4)$$

The equilibrium constants were determined at different temperatures, thus allowing the heats of reaction to be estimated. Reaction 2 was slightly exothermic, ΔH_2^0 being —2.3 kcal mol^{-1}; all other reactions were endothermic with reaction enthalpies of $\Delta H_1^0 = 1.2$, $\Delta H_3^0 = 8.4$ and $\Delta H_4^0 = 5.4$ kcal mol^{-1}, respectively.

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[*] For Part I see ref. 16.

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Introduction

After the initial report by Slaugh and Mullineaux [1] that modification of the traditional cobalt tetracarbonyl catalyst with tri-n-butylphosphine gave a considerable improvement in catalyst performance for the hydroformylation of olefins, much work was devoted to the study of the effects of a variety of organo-phosphines and phosphites [2], for example, in attempts to correlate catalyst performance with the properties of the complementary ligand, viz. basicity and steric hinderance.

Despite the tremendous body of work performed, the appearance of the catalyst system under technical hydroformylation conditions remained speculative and was only tentatively interpreted from the trends observed in hydroformylation rate and selectivity with gross catalyst composition. This was mainly due to the lack of appropriate analytical techniques operative under industrial hydroformylation conditions. In recent years several high temperature—pressure spectroscopic cells have been developed [3] which make possible the in situ analysis of the catalyst system and other reaction intermediates by IR spectroscopy.

Using these techniques related data were obtained by Whyman about $Co_2(CO)_8$ at high temperature and pressure of CO [4]. Some data concerning the cobalt carbonyl—tributylphosphine system were reported by Bianchi et al. [6], Whyman [5] and Pregaglia [7], although the latter data were not obtained under truly in situ conditions because samples were quenched in a room temperature/pressure IR cell.

Systematic data on the appearance of the cobalt carbonyl—PBu_3 and other catalyst combinations in relation to the reaction parameters are still lacking but are essential for a fundamental understanding of the influence of the complementary ligands on catalyst performance. As a contribution to this study and a continuation of the work previously published [16], the cobalt carbonyl—PBu_3 system, dissolved in n-heptane and in the absence of olefin, has been investigated for a range of reaction conditions, such as temperature, partial pressure of hydrogen and of carbon monoxide and the phosphorus-to-cobalt ratio.

Experimental

The experiments were carried out in an electrically heated 1 liter AISI 316 SS autoclave (Andreas Hofer), equipped with a magnedrive impeller type stirrer, and connected by means of a capillary line to a high pressure/temperature IR spectroscopic cell of the type as described previously [3]. The temperature of liquid autoclave contents, line and cell were measured with calibrated chromel—alumel thermocouples and controlled to within 1°C, all at the same temperature.

The autoclave was connected to several component supply systems, viz. a 45 ml high-pressure tank for injection of catalyst solution or complementary ligands and high-pressure tanks, equipped with pressure control valves, containing hydrogen and carbon monoxide so that the partial pressure of each could be adjusted independently while the reactions in the autoclave were in progress.

After the components were added and the partial pressures sèt, the autoclave was left for several hours at the desired temperature under vigorous stirring to establish equilibrium conditions. A sample from the autoclave contents was transferred to the cell by slowly opening a high pressure valve downstream of the cell so that the confined sample always remained under the same temperature and pressure. During a run several samples were taken to check for steady state conditions in the autoclave. The samples confined in the cell were collected separately after measurement, stored under atmospheric CO, and sometimes recorded at ambient conditions for comparison with spectra obtained in situ. As a modification to the system previously discussed the window aperture was enlarged from 4 to 6 mm diameter. This gave an increase in radiation transmission to 30% and a more favourable spectral resolution. The spectra were recorded with a Perkin—Elmer type 357 grating IR spectrometer, with the solvent confined in a normal type of cell as reference. Usually 400 ml of n-heptane (Baker, 99% purity) was charged to the autoclave as a solvent. It was stored over activated molecular sieves. Dicobalt octacarbonyl was prepared according to the method of Szabó et al. [8]. After double recrystallisation from dichloromethane the purity, as determined by complexometric cobalt determination [9], was 97-98 wt%.

Tri-n-butylphosphine (Fluka, 98% purity) was distilled in argon and stored over activated molecular sieves. Hydrogen (Loos & Co.) was deoxidised and dried prior to use, while carbon monoxide (Loos & Co.) was used without pretreatment. All experiments were done with comparatively low concentrations of dicobalt octacarbonyl of approximately 2 mmol l^{-1} (~ 0.7 g l^{-1}). The concentration of the different catalyst species was found from absorptivity measurements at characteristic frequencies. The calibration was obtained from test mixtures prepared at reaction conditions by a systematic step procedure. Starting from a $Co_2(CO)_8$ solution with known concentration (calibration at 2078 cm^{-1}) PBu_3 was added. From the decrease in $Co_2(CO)_8$ the amount of $Co_2(CO)_7$-PBu_3 was calculated and related to the absorptivity of the same compound at 1992 cm^{-1}. In a similar way $HCo(CO)_4$ was calibrated at 2055 cm^{-1} from a $Co_2(CO)_8$ solution and subsequent addition of hydrogen. Calibration of $HCo(CO)_3PBu_3$ at 1970 cm^{-1}, was accomplished by addition of hydrogen to a $Co_2(CO)_8$—PBu_3 solution. The following absorptivity coefficients ϵ (relative to $Co_2(CO)_8$) were obtained: $Co_2(CO)_8$, 1.0; $HCo(CO)_4$, 0.5; $Co_2(CO)_7PBu_3$, 1.8 and $HCo(CO)_3PBu_3$, 0.4.

Previous infrared data for cobalt carbonyl complexes in heptane are summarized in Table 1.

TABLE 1

SUMMARY OF PUBLISHED DATA ON VIBRATION FREQUENCIES OF COBALT CARBONYL COMPLEXES IN HEPTANE

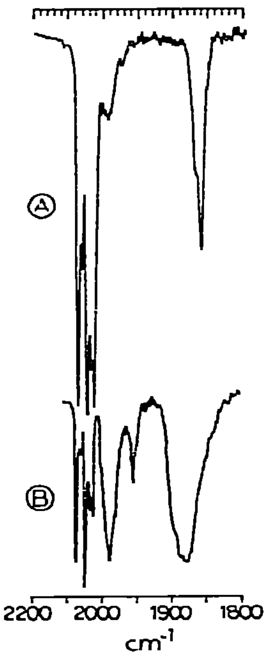
Compound	Vibration frequencies (cm^{-1})	Ref.
$Co_2(CO)_8$ (bridged)	2112, 2071, 2044, 2042, 1866, 1857	15
$Co_2(CO)_8$ (non-bridged)	2107, 2069, 2031, 2023	15
$Co_2(CO)_7PBu_3$	2078 m, 2022 m, 2005 (sh), 1992 vs, 1955 w	12
$Co_2(CO)_6(PBu_3)_2$	1972 m (sh), 1953 vs, 1927 w (sh)	16
$[Co(CO)_3(PBu_3)_2]^+[Co(CO)_4]^-$	1990-2000 vs, 1885 vs	7, 16
$HCo(CO)_4$	2118 w, 2055 m, 2032 vs, 1995 vw	17
$HCo(CO)_3PBu_3$	2049 mw, 1970 vs, 1935 w	16
$HCo(CO)_2(PBu_3)_2$	1978-1976 s, 1958 s, 1942 w, 1912 (sh), 1902 vs	18

Results

The changes in the IR spectrum of a solution of $Co_2(CO)_8$ in n-heptane due to the addition of PBu_3 at room temperature and 1 atm of CO are illustrated in Fig. 1. The new absorption bands are characteristic for the ionic species $[Co(CO)_3(PBu_3)_2]^+$ $[Co(CO)_4]^-$ (1990, 1880 cm^{-1}) and the covalent species $Co_2(CO)_6(PBu_3)_2$ (1995 cm^{-1}). Identical findings were reported by Manning [10] with benzene as a solvent. The presence of absorption bands between 2000 and 2100 cm^{-1} characteristic of $Co_2(CO)_8$ clearly shows that the reactions do not go to completion at ambient temperature, even in the presence of excess PBu_3.

An increase of the CO pressure does not cause drastic changes in the composition of the carbonyl complexes (Fig. 2). At 40°C, a P-to-Co ratio of 1 and a CO pressure of 7 or 31 atm the major fraction of $Co_2(CO)_8$ remains unconverted while only small concentrations of the two liganded complexes mentioned above are present. (In Fig. 2 the broad band above 2100 cm^{-1} is caused by dissolved CO).

An increase of the temperature to 81° and 100°C results in a strong increase of the 1992 cm^{-1} absorption, a small but significant shift of the 1953 cm^{-1} absorption to 1957 cm^{-1} and the disappearance of the 1885 cm^{-1} absorption. This is all indicative of the presence of only $Co_2(CO)_7PBu_3$ besides unconverted $Co_2(CO)_8$. The reversibility of the system proved to be very poor, because subsequent cooling of the solution to room temperature did not result in re-formation of either ionic or disubstituted species. Even after 50 h, with a P-to-Co ratio



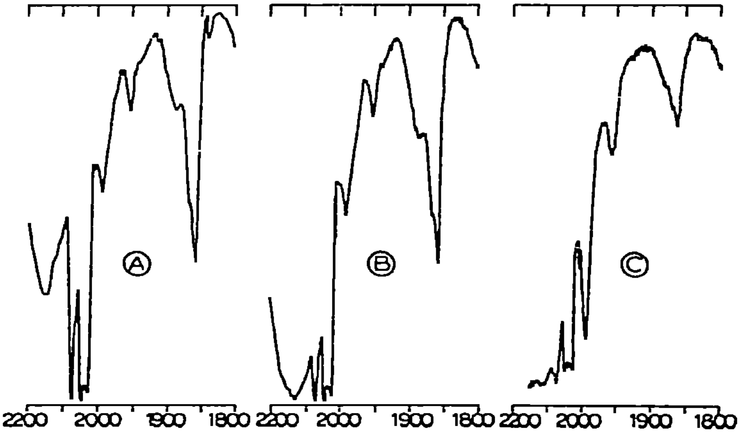


Fig. 1. IR spectra (cm^{-1}): A, $Co_2(CO)_8$; B, $Co_2(CO)_8$ + PBu_3. P/Co > 5, temperature 20°C, 1 atm CO.

Fig. 2. IR spectra (cm^{-1}): $Co_2(CO)_8$—PBu_3 in heptane, P/Co = 1. A, 40°C, 7 atm CO; B, 40°C, 31 atm CO; C, 100°C, 36 atm CO.

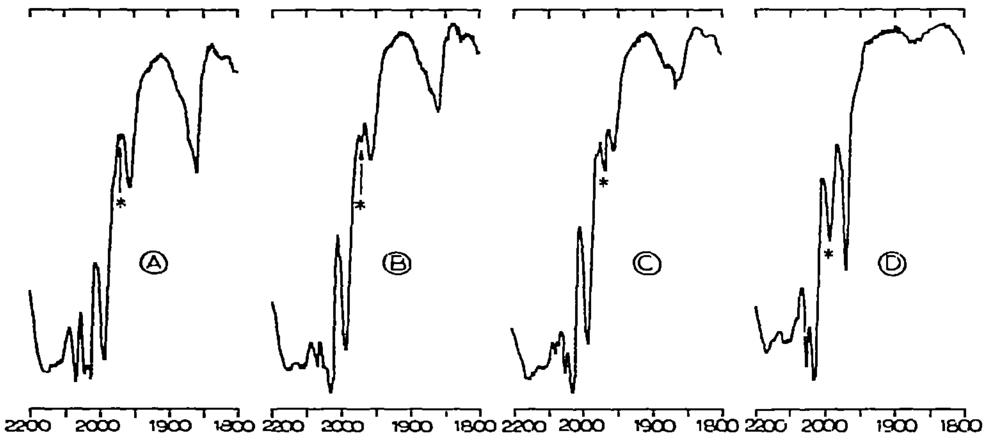


Fig. 3. IR spectra (cm^{-1}): addition of hydrogen to $Co_2(CO)_8$—PBu_3 in heptane. P/Co = 5. A, no hydrogen, 98°C, 20 atm CO, at zero time addition of 60 atm H_2; B, after 35 min, rest idem; C, after 60 min, rest idem; D, 149°C, 60 atm H_2, 20 atm CO.

of 5 and at 30 atm of CO, the spectrum indicated only $Co_2(CO)_7PBu_3$ and $Co_2(CO)_8$. Even after release of CO to 1 atm and equilibration for 24 h the two complexes were still present, but with a slightly higher concentration of $Co_2(CO)_7PBu_3$. Addition of hydrogen to the system brings new absorption bands in the IR spectrum. They indicate the formation of $HCo(CO)_4$ and $HCo(CO)_3PBu_3$, both at slow rates at 100°C. This is illustrated in Fig. 3, which shows that a steady state spectrum is not found within 35 minutes following

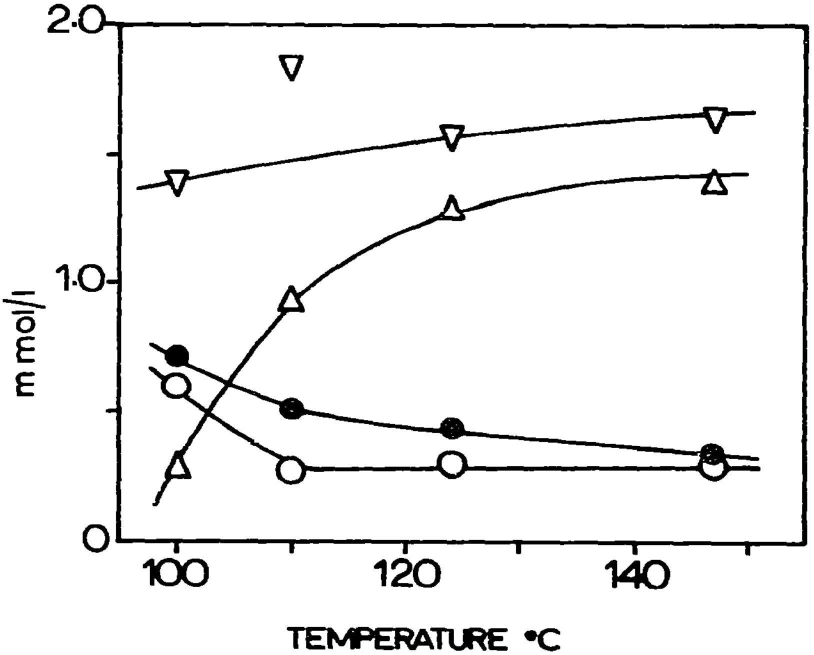
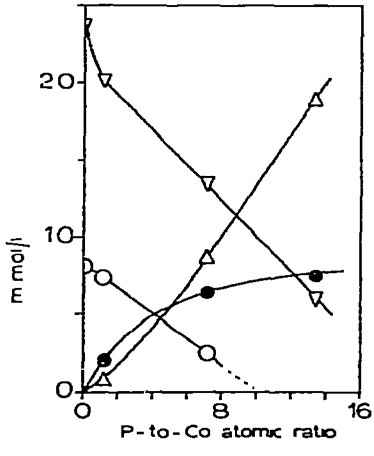


Fig. 4. Effects of temperature on $[Co_2(CO)_8]$. Initial conc. of $Co_2(CO)_8$ = 2.16 mmol l^{-1}, PBu_3 = 21.8 mmol l^{-1}, 20 atm CO, 60 atm H_2; ▽ $HCoCO_4$, △ $HCoCO_3PBu_3$, ○ Co_2CO_8, ● $Co_2CO_7PBu_3$.

hydrogen addition. A gradual increase of the $HCo(CO)_3PBu_3$ absorption band (1970 cm^{-1}, marked * in Fig. 3), with time, a slow decrease of the bridged carbonyl vibrations of $Co_2(CO)_8$ (1860 cm^{-1}) and a parallel increase of the $HCo(CO)_4$ absorption band (2032, 2055 cm^{-1}) are observed. Under almost the whole range of reaction conditions investigated the equilibrium composition consisted only of $Co_2(CO)_8$, $Co_2(CO)_7PBu_3$, $HCo(CO)_4$ and $HCo(CO)_3PBu_3$. The concentration ratio of the several species was found to depend on parameters, such as temperature, partial pressure of CO and H_2 and P-to-Co ratio. As can be seen from Fig. 4, the hydrido species are preferred at higher temperatures, but with a P-to-Co ratio of 5, the concentration of $HCo(CO)_4$ is still higher than that of $HCo(CO)_3PBu_3$. This is also clearly illustrated in Fig. 5 where the carbonyl composition is plotted vs. the P-to-Co ratio. Addition of PBu_3 in stoichiometric proportions to cobalt carbonyl results in only 12% of the cobalt being present in substituted carbonyls. Only at P-to-Co ratios higher than 10 is unsubstituted $Co_2(CO)_8$ almost undetectable and the $HCo(CO)_3PBu_3$ concentration increases above that of $HCo(CO)_4$. Under these conditions the occurrence of a weak 1904 cm^{-1} absorption indicates the presence of low concentrations of $HCo(CO)_2(PBu_3)_2$ (not shown in Fig. 5). After cooling of this reaction mixture and release of pressure, the IR spectrum indicated the presence of the sole component $Co_2(CO)_7PBu_3$, most probably formed by recombination of $HCo(CO)_3PBu_3$ and $HCo(CO)_4$. This opened a simple new route for direct synthesis of the same compound in contrast to the method of Szabó [11].

Increase of the hydrogen pressure favours the formation of $HCo(CO)_3PBu_3$ over all other species (see Fig. 6). The simultaneous steep decrease of $Co_2(CO)_8$ and $HCo(CO)_4$ concentrations, which reach a steady level at relatively low hydrogen pressures, leads to the conclusion that $HCo(CO)_3PBu_3$ is not only formed by reaction of $Co_2(CO)_7PBu_3$ with H_2 but more significantly by direct substitution of $HCo(CO)_4$ [from $Co_2(CO)_8$ and H_2] with PBu_3.



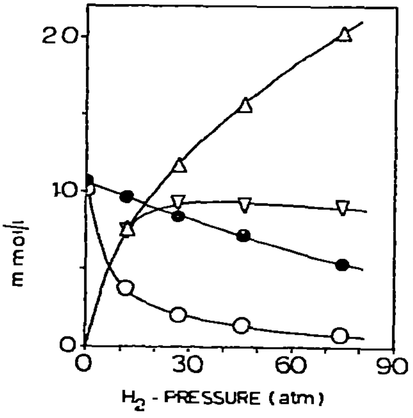
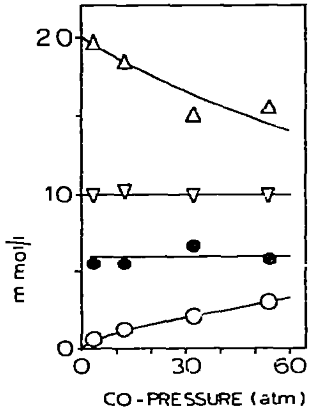


Fig. 5. Effects of P-to-Co ratio. Initial conc. of $Co_2(CO)_8$ = 2.0 mmol l^{-1}, 26 atm CO, 42 atm H_2, temperature 102°C; symbols as Fig. 4.

Fig. 6. Effects of H_2 pressure. Initial conc. of $Co_2(CO)_8$ = 2.08 mmol l^{-1}, PBu_3 = 25.0 mmol l^{-1}, 29.5 atm CO, temperature 100°C; symbols as Fig. 4.



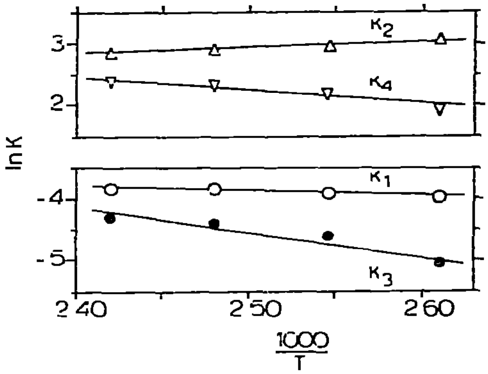


Fig. 7. Effects of CO pressure. Initial conc. of $Co_2(CO)_8$ = 2.08 mmol l^{-1}, PBu_3 = 25.8 mmol l^{-1}, 56 atm H_2, temperature 100°C; symbols as Fig. 4.

Fig. 8. Correlation of K-values and temperature.

Finally the effect of the CO pressure is minimal. It results merely in an increasing $Co_2(CO)_8$ concentration at the cost of $HCo(CO)_3PBu_3$, while $Co_2(CO)_7PBu_3$ and $HCo(CO)_4$ are essentially not affected (Fig. 7).

The results obtained suggest that the following equilibria are operative:

$$Co_2(CO)_8 + H_2 \overset{K_1}{\rightleftharpoons} 2HCo(CO)_4 \qquad (1)$$

$$Co_2(CO)_8 + PBu_3 \overset{K_2}{\rightleftharpoons} Co_2(CO)_7PBu_3 + CO \qquad (2)$$

$$Co_2(CO)_7PBu_3 + H_2 \overset{K_3}{\rightleftharpoons} HCo(CO)_3PBu_3 + HCo(CO)_4 \qquad (3)$$

$$HCo(CO)_4 + PBu_3 \overset{K_4}{\rightleftharpoons} HCo(CO)_3PBu_3 + CO \qquad (4)$$

In testing the consistency of these equations, values of the equilibrium constants were calculated from data measured at variable P-to-Co ratios. They were found to be independent of this ratio indicating that eqns. 1 to 4 represent a fair interpretation of all interchanges occurring. The concentration of the components involved was found as follows: the concentration of the carbonyl species resulted from IR spectral data; the concentration of unconverted PBu_3 was found as the difference between the amount added initially and the concentration of PBu_3-liganded carbonyls; for the concentration of hydrogen and carbon monoxide, solubility data were used. They were determined in separate experiments by measuring the volume of gas given off at normal pressure by a sample taken from n-heptane which was equilibrated with hydrogen or carbon monoxide at different temperatures. The data exhibited good agreement with extrapolation from the data reported by Ungvary [12].

Following the same procedure the equilibrium concentrations of the other components, and the equilibrium constants derived therefrom, were found at different temperatures.

The data listed in Table 2 are plotted in Fig. 8 and from the straight lines

TABLE 2

DERIVATION OF EQUILIBRIUM CONSTANTS

	Concentration (mmol l^{-1}) and K values at:			
	110°C	120°C	130°C	140°C
$Co_2(CO)_8$	0.27	0.27	0.27	0.27
$Co_2(CO)_7PBu_3$	0.5	0.43	0.38	0.35
$HCo(CO)_4$	1.47	1.54	1.60	1.63
$HCo(CO)_3PBu_3$	0.93	1.2	1.34	1.39
PBu_3	20.37	20.17	20.08	20.06
H_2	424	439	459	479
CO	226	251	262	272
K_1 (× 10^2)	1.88	2.0	2.07	2.06
K_2	20.5	19.8	18.4	17.6
K_3 (× 10^2)	0.64	0.98	1.23	1.35
K_4	7.0	9.7	10.9	11.6

$$K_1 = \frac{[HCo(CO)_4]^2}{[H_2][Co_2(CO)_8]};\ K_2 = \frac{[CO][Co_2(CO)_7PBu_3]}{[Co_2(CO)_8][PBu_3]};\ K_3 = \frac{[HCo(CO)_3PBu_3][HCo(CO)_4]}{[Co_2(CO)_7PBu_3][H_2]};$$

$$K_4 = \frac{[CO][HCo(CO)_3PBu_3]}{[PBu_3][HCo(CO)_4]}$$

the following thermodynamic data were estimated: $\Delta H_1^0 = 1.2$, $\Delta H_2^0 = -2.3$, $\Delta H_3^0 = 8.4$, $\Delta H_4^0 = 5.4$ kcal mol^{-1}; $\Delta S_1 = -4.8$, $\Delta S_2 = 0.1$, $\Delta S_3 = 12.6$, and $\Delta S_4 = 17.7$ kcal mol^{-1} K^{-1}.

The heats of formation of $HCo(CO)_4$, $Co_2(CO)_7PBu_3$ and $HCo(CO)_3PBu_3$ can be estimated from literature. As $\Delta H_f^0[Co_2(CO)_8]$ is taken as −298.8 kcal mol^{-1} [13], it follows from the value of ΔH_1^0 that $\Delta H_f^0[HCo(CO)_4] = -149$ kcal mol^{-1}. Furthermore, if $\Delta H_f^0[PBu_3]$ is taken as 122.9 [14], $\Delta H_f^0[Co_2(CO)_7PBu_3] = -152$ and $\Delta H_f^0[HCo(CO)_3PBu_3] = 5.4$ kcal mol^{-1}.

Discussion

The thermodynamic data obtained indicate reactions 1, 3 and 4 to be endothermic. Reaction 1, the split-up of $Co_2(CO)_8$ into $HCo(CO)_4$, was studied before by Ungvary [12], who also found a low endothermic heat effect. The exchange of a CO ligand from $Co_2(CO)_8$ by a PBu_3 ligand (reaction 2) is slightly exothermic. The result is that an increase of the temperature will favour a further shift to the right of equilibria 1, 3 and 4 and a decrease of $[Co_2(CO)_7PBu_3]$. Because of the relatively high endothermicity of reactions 3 and 4 the equilibrium composition will shift ultimately to $HCo(CO)_3PBu_3$ as sole component, provided sufficient hydrogen is available for complete conversion of $Co_2(CO)_8$ into $HCo(CO)_4$. Consequently, effects of PBu_3-liganded hydridocobalt carbonyl catalysts can be seen only under specific reaction conditions, viz. high temperature, high partial pressure of hydrogen, low stoichiometric P-to-Co ratio and low carbon monoxide pressure. One can see that in a wide range of conditions the catalyst is vaguely defined and a considerable part of the cobalt is present as inactive dicobalt carbonyl and non-liganded hydridocarbonyl. Obviously this will influence the catalytic performance and evidence for this phenomenon has also been found in ref. 15. The effects reported therein on the hydroformylation rate and selectivity with the change of P-to-Co ratio and partial pressures can be explained fully in the light of the findings reported above. However, the results are different from the single data points reported by other authors. Thus Pregaglia et al. [7] stated that only $Co_2(CO)_6(PBu_3)_2$ and $HCo(CO)_3PBu_3$ are present at 140°C, a P-to-Co ratio of 2.2 and partial pressures of carbon monoxide and hydrogen of approximately 20 atm; the second complex was presumably formed from the first by the action of hydrogen. Bianchi et al. [6] found an equilibrium mixture consisting of $Co_2(CO)_6(PBu_3)_2$, $Co_2(CO)_7PBu_3$, $HCo(CO)_3PBu_3$ and $HCo(CO)_4$ at 100°C, a hydrogen pressure of 50 atm and a carbon monoxide pressure ranging from 3 to 70 atm.

Most probably the explanation can be found in the cobalt concentration, which was quite different in the three studies; e.g. Pregaglia et al. used cobalt concentrations of 4 g l^{-1}, Bianchi et al. 0.6 g l^{-1}, while only 0.1 g l^{-1} was used in this work. There is an interesting correlation between the cobalt concentration and the degree of PBu_3 substitution of the species. The higher the former, the higher the concentration of PBu_3-liganded complexes. In fact equilibria 1 to 4 suggest the same trend. With higher amounts of cobalt the importance of dissolved carbon monoxide, which shifts the equilibria in the reverse direction, decreases and will favour PBu_3-liganded species. Under the conditions in this work no evidence was obtained, however, for $Co_2(CO)_6(PBu_3)_2$ being present, so apparently this reaction becomes significant only at much higher cobalt concentrations.

In the light of these results it remains questionable whether $HCo(CO)_3PBu_3$ can be formed directly from $Co_2(CO)_6(PBu_3)_2$ as Pregaglia et al. [7] proposed, or whether, at high cobalt concentrations, this interchange also proceeds via $Co_2(CO)_7PBu_3$ as outlined in this paper. It will be appreciated that the usual industrial conditions for hydroformylation differ somewhat from the conditions used in the present investigation. Although the catalyst composition in the technical oxo temperature range of 170-190°C could be found by extrapolation of the present data, it must be realized that the cobalt concentration in the industrial oxo processes is much higher than in this work. The effect of this on the catalyst composition has not been studied as yet; it may influence the degree of ligand exchange of the different species in the way outlined in the proceeding paragraph. Another aspect is the effect of the olefin on the distribution of the various cobalt carbonyl species; as has been reported recently, the ratios of the different species changes profoundly during the olefin addition, but tend to revert to the original values as the conversion proceeds [16, 17]. However, interpretation of these effects involves the kinetics of the succesive elementary reactions taking place in the hydroformylation rather than the thermodynamic aspects of the cobalt carbonyl-PBu_3 system which we have studied.

Acknowledgements

The authors are indebted to J.M. Alberigs and H. Pleiter for the construction of the apparatus and assistance in the experimental work. Professor E. Oltay is acknowledged for his initiative, which resulted in this work.

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