Organometallics **1997,** *16,* 4235−4236 4235

Cobalt-Catalyzed Hydroformylation of Olefins in the Presence of Additional "Inert" Gases

Franco Piacenti,*,[†] Fausto Calderazzo,[‡] Mario Bianchi,[†] Luca Rosi,[†] and Piero Frediani[†]

Dipartimento di Chimica Organica "Ugo Schiff", Università di Firenze, Via G. Capponi 9, I-50121 Firenze, Italy, and Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy

Received June 6, 1997[⊗]

Summary: The rate of hydroformylation of cyclohexene to cyclohexanecarboxaldehyde in the presence of octacarbonyldicobalt is strongly reduced by the presence of an additional gas, such as dinitrogen or argon, under very high pressure, other conditions being kept constant. Competition of these gases with dihydrogen and/or the olefin within the coordination sphere of the catalytically active cobalt carbonyl species is suggested to be responsible for the observed behavior.

Dinitrogen[1] and dihydrogen[2] complexes are well-established in the literature, and also C−H σ-complexes have been detected spectroscopically.[3] Moreover, agostic M···H−C interactions[4] have been suggested to play an important role in the catalytic processes, especially in polymerization reactions.[5] Preliminary data on xenon metal complexes have also been reported.[6]

The rate of hydroformylation of cyclohexene catalyzed by cobalt carbonyls decreases by increasing the partial pressure of carbon monoxide above a threshold value.[7] This behavior, once hydro-, alkyl-, and acylcobalt carbonyls became accepted intermediates of this reaction, has been interpreted as being due to the competition between CO and alkene and/or dihydrogen for the coordinatively unsaturated species, thus affecting the reaction rate. In this connection, it is worth mentioning that even a small carbon monoxide pressure (as low as a 0.02 mol fraction) has a retarding effect[8a] on the formation of tetracarbonylcobalt hydride from octacarbonyldicobalt and dihydrogen.

$$RCo(CO)_4 \rightleftharpoons RCo(CO)_3 + CO$$

$$R = Co(CO)_4;\ H;\ alkyl,\ acyl$$

The elementary steps normally accepted to be involved in the hydroformylation reaction may be sum-

---

[†] Università di Firenze.

[‡] Università di Pisa.

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1997.

(1) (a) Sacco, A.; Rossi, M. *J. Chem. Soc., Chem. Commun.* **1967**, 316. (b) Jolly, P. W.; Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1968**, *80*, 705. (c) Aresta, M.; Giannoccaro, P.; Rossi, M.; Sacco, A. *Inorg. Chim. Acta* **1971**, *5*, 203. (d) Banister, J. A.; George, M. W.; Grubert, S.; Howdle, S. M.; Jobling, M.; Johnson, F. P. A.; Morrison, S. L.; Poliakoff, M.; Schubert, U.; Westwell, J. R. *J. Organomet. Chem.* **1994**, *484*, 129. (e) Gambarotta, S. *J. Organomet. Chem.* **1995**, *500*, 117. (f) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115. (g) Bazhenova, T. A.; Kulikov, A. V.; Shestakov, A. F.; Shilov, A. E.; Antipin, M. Yu.; Lyssenko, K. A.; Struchkov, Yu. T.; Makhaev, V. D. *J. Am. Chem. Soc.* **1995**, *117*, 12176.

(2) (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Gonzales, A. A.; Zhang, K.; Nolan, S. P.; Lopez de la Vega, R.; Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J. *Organometallics* **1988**, *7*, 2429. (c) Haward, M. T.; George, M. W.; Howdle, S. M.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1990**, 913. (d) Heinekey, D. M.; Oldham, W. J. *Chem. Rev.* **1993**, *93*, 913. (e) Sabo-Etienne, S.; Chaudret, B.; el Makarim, H. A.; Barthelat, J.-C.; Daudey, J.-P.; Moïse, C.; Leblanc, G. J. *J. Am. Chem. Soc.* **1994**, *116*, 9335. (f) Kubas, G. J.; Nelson, J. E.; Bryan, J. C.; Eckert, J.; Wisniewski, L.; Zilm, K. *Inorg. Chem.* **1994**, *33*, 2954. (g) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 11584. (h) Li, J.; Dickson, R. M.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 11482. (i) Ma, B.; Collins, C. L.; Schaefer H. F., III. *J. Am. Chem. Soc.* **1996**, *118*, 870. (j) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1992**, *114*, 5905. (k) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548. (l) Bianchini, C.; Farnetti, E.; Graziani, M.; Kaspar, J.; Vizza, F. *J. Am. Chem. Soc.* **1993**, *115*, 1753. (m) Heinekey, D. M.; Liegeois, A.; van Roon, M. *J. Am. Chem. Soc.* **1994**, *116*, 8388. (n) Gusev, D. G.; Notheis, J. U.; Rambo, J. R.; Hauger, B. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 7409.

(3) (a) Billups, W. E.; Chang, S.-C.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 2039. (b) Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987. (c) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332. (d) Graham, M. A.; Perutz, R. N.; Poliakoff, M.; Turner, J. J. *J. Organomet. Chem.* **1972**, *34*, C34. (e) Welch, J. A.; Peters, K. S.; Vaida, V. *J. Phys. Chem.* **1982**, *86*, 1941.

(4) (a) Cotton, F. A.; LaCour, T.; Stanislowski, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 754. (b) Cotton, F. A.; Stanislowski, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 5074. (c) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (d) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(5) (a) Laverty, D. T.; Rooney, J. J. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 869. (b) Krauledat, H.; Brintzinger, H. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1412. (c) Clawson, L.; Soto, J.; Buchwald, S. L.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 3377. (d) Brookhardt, M.; Volpe, A. F. Jr.; Lincoln, D. M.; Horvàth, I. T.; Millar, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 5634. (e) Janiak, C. *J. Organomet. Chem.* **1993**, *452*, 63. (f) Pellecchia, C.; Grassi, A.; Zambelli, A. *Organometallics* **1994**, *13*, 298. (g) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (h) Leclerc, M. K.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1995**, *117*, 1651. (i) Støvneng, J. A.; Rytter, E. *J. Organomet. Chem.* **1996**, *519*, 277. (j) Fan, L.; Krzywicki, A.; Somogyvari, A.; Ziegler, T. *Inorg. Chem.* **1996**, *35*, 4003.

(6) (a) Simpson, M. B.; Poliakoff, M.; Turner, J. J.; Maier, W. B.; McLuaghlin, I. G. *J. Chem. Soc., Chem. Commun.* **1983**, 1355. (b) Wells, J. R.; Weitz, E. *J. Am. Chem. Soc.* **1992**, *114*, 2783. (c) Weiller, B. H. *J. Am. Chem. Soc.* **1992**, *114*, 10910. (d) Bengali, A. A.; Bergman, R. G.; Moore, C. B. *J. Am. Chem. Soc.* **1995**, *117*, 3879.

(7) (a) Calderazzo, F.; Ercoli, R.; Natta, G. Metal Carbonyls: Preparation, Structure and Properties. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Interscience Publishers: New York, London, and Sidney, 1967; Vol. 1. (b) Natta, G.; Ercoli, R. *Chim. Ind. (Milan)* **1952**, *34*, 503. (c) Natta, G.; Ercoli, R.; Castellano, S.; Barbieri, F. H. *J. Am. Chem. Soc.* **1954**, *76*, 4049. (d) Natta, G.; Ercoli, R.; Castellano, S. *Chim. Ind. (Milan)* **1955**, *37*, 6. (e) Pino, P.; Piacenti, F.; Bianchi, M. Reactions of Carbon Monoxide and Hydrogen with Olefinic Substrates: The Hydroformylation (OXO) Reactions. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Interscience Publishers: New York, London, and Sidney, 1977; Vol. 2, pp 43−231. (f) Piacenti, F.; Bianchi, M. Carbonylation of Saturated Oxygenated Compounds. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Interscience Publishers: New York, London, and Sydney, 1977; Vol. 2, pp 1−42. (g) Martin, A. R. *Chem Ind. (London)* **1954**, 1536. (h) Greenfield, H.; Metlin, S.; Wender, I. *Abstracts of Papers*, 126th Meeting of the American Chemical Society, New York, September 12−17, 1954; American Chemical Society: Washington, DC, 1954.

(8) (a) Pino, P.; Ercoli, R.; Calderazzo, F. *Chim. Ind. (Milan)* **1955**, *37*, 782. (b) Ungváry, F. *J. Organomet. Chem.* **1972**, *36*, 363. (c) Alemdaroglu, N. H.; Penninger, J. M.; Oltay, E. *Monatsh. Chem.* **1976**, *107*, 1043. (d) For a more recent study of the equilibrium in supercritical carbon dioxide by ^1H and ^{59}Co NMR spectrometry under pressure, see: Rathke, J. W.; Klinger, R. J.; Krause, T. R. *Organometallics* **1992**, *11*, 585.

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

S0276-7333(97)00471-8 CCC: $14.00

marized as follows: (a) conversion of octacarbonyldicobalt to the corresponding hydrido species, (b) olefin addition to the hydride to form the alkyl derivative, (c) carbonyl insertion to give the corresponding acyls, and (d) hydrogenolysis of the acyls to the products.

In view of the new findings on nonclassical molecular complexes and the possibility that dihydrogen complexes might be involved in the preliminary steps of the process, it was believed to be worthwhile to re-examine the rate of the hydroformylation reaction in the presence of gases which, although not able to interfere with the thermodynamics of the process, could potentially modify its kinetics due to their competing activity in the equilibria presumably involved in some of the primary steps. In this connection, it is relevant to recall that dinitrogen and dihydrogen compete with each other for the coordination sphere of cobalt(I) in the $CoH_3(PR_3)_3$/$Co(N_2)H(PR_3)_3$ system, as established by Sacco and Rossi.[1a] The rearrangement from the starting $CoH_3(PR_3)_3$ to the final $Co(N_2)H(PR_3)_3$ involves an equilibrium reaction presumably characterized by a small entropy change. Moreover, the dihydrogen complex $Co(H_2)H(CO)_3$ has been detected[9] among the products formed by photolysis of $H-Co(CO)_4$ in a H_2/Ar matrix.

If this were true under hydroformylation conditions and the key intermediate for the activation of dihydrogen (and/or the olefin) could be intercepted by an additional component of the system like dinitrogen, a sufficient concentration of this gas, or any other gas with analogous properties, might affect the reaction rate to a detectable extent.

We have, therefore, investigated the influence of dinitrogen and argon on the rate of hydroformylation of cyclohexene[10] by performing experiments[11] in which dinitrogen[12] or argon were introduced, after the usual carbon monoxide and dihydrogen mixture, to cause an additional pressure increase in the range between 500 and 1000 bar.

We have in fact determined the olefin conversion to aldehyde in isochronous (3 h) and isothermal (373 K) hydroformylation experiments in which, other conditions being maintained constant, an elevated pressure of an additional gas is introduced, see Table 1. The olefin conversion is strongly reduced by the presence of relevant amounts of dinitrogen in solution. The gas solubility and the corresponding volume increase due to the additional gas (at 373 K under a pressure of 1000 bar, dissolved dinitrogen increases the volume of the solvent by about 15%) were considered as a possible explanation for the lower yields: such a dilution of reagents and catalyst, mimicked by the addition of an equivalent amount of solvent, in fact, caused a yield decrease from 30 to 29%, thus confirming that a specific effect of dinitrogen must be operating on a molecular basis in our experiments. The solubilities of argon and dinitrogen in toluene,[13] expressed as a mole fraction at 298 K, are 10.86×10^{-4} and 5.74×10^{-4}, respectively; thus, the solubility of argon should be expected to be at least twice that of dinitrogen. Due to the different compressibilities, the results obtained with the two gases are not directly comparable. However, there is no doubt that argon causes a similar effect as dinitrogen does under similar experimental conditions. We believe that at the moment the most plausible explanation of the observed experimental facts is a competition effect by dinitrogen or argon for the coordination site within the catalytically active species.

Table 1. Hydroformylation of Cyclohexene in the Presence of Dinitrogen or Argon. Conversion (%) to Cyclohexanecarboxaldehyde[a]

additional gas used	pressure of additional gas (bar)			
	0	500	800	1000
N_2	30	22 (581)	17 (757)	12 (1039)
Ar	30	19 (530)	10 (802)	9 (1015)

[a] The manometric pressure reading of the additional gas is reported in parentheses. Experimental conditions: toluene, 7 mL; $Co_2(CO)_8$, 51 mg (0.149 mmol); cyclohexene, 500 mg (6.15 mmol); p_{CO}, 70 ± 1 bar at 373 K; p_{H_2}, 85 ± 2 bar at 373 K; reaction time, 3 h; temperature, 373 K.

Acknowledgment. We are indebted to the Ministero della Ricerca Scientifica e Tecnologica (MURST) for financial support.

OM9704713

---

(9) Sweany, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 3739. Sweany, R. L.; Russel, F. N. *Organometallics* **1988**, *7*, 719.

(10) Cyclohexene, Fluka reagent grade, was eluted through activated Al_2O_3 and distilled under dinitrogen before use, bp 356 K. C. Erba reagent grade toluene was refluxed over sodium and distilled under dinitrogen before use.

(11) The hydroformylation experiments were performed in a stainless steel rocking autoclave, 25 mL capacity, capable of withstanding a pressure of several thousand bar, electrically heated with a temperature control (±1 K). Pressures were measured with a transducer with an accuracy of ±1 bar (transducer model Z Absolute, Sensotec). Molar ratios of liquid and gaseous reagents were chosen in such a way as to avoid a relevant pressure decrease. Solid catalyst was introduced under dinitrogen into the autoclave, which was then evacuated; solvent and olefin were introduced by suction, and then carbon monoxide was pressurized up to 5 bar. Rocking and heating were then started, and at 373 K the carbon monoxide pressure was increased to 70 atm. Within 1 min, dihydrogen up to a total pressure of 160 bar (85 ± 2 bar of dihydrogen from control experiments) and the additional gas up to the required pressure (see Table 1) were introduced into the still autoclave, which was rocked again immediately after. After 3 h, the autoclave was rapidly cooled by immersion into water. Gases were vented through a condenser, and the clear yellow solution was subjected to GLC chromatography to determine the conversion to cyclohexanecarboxaldehyde based on both residual cyclohexene and formed aldehyde. Olefin hydrogenation was always low, below 1%. Compressibilities of both dinitrogen and argon were estimated, with an accuracy sufficient for our purpose, by volumetric measurements, as a function of pressure, of the gas released at atmospheric pressure from an empty autoclave maintained at 373 K. Similar experiments performed in the presence of a known volume of solvent provided sufficient data for an evaluation of the amount of dissolved gas.

(12) Dinitrogen (99.996% pure), argon, (99.998% pure), CO (99.3% pure), and hydrogen (99.85% pure) were supplied by SOL. Octacarbonyldicobalt, supplied by Strem Chemicals, was recrystallized before use.

(13) Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1.