Cobalt-Catalyzed Hydroformylation of Olefins in the Presence of Xenon: New Experimental Evidence for Metal–Xenon Adducts

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Keywords: Hydroformylations / Rare gas / Homogeneous catalysis / Carbonylcobalt compounds

The rate of cobalt-catalyzed hydroformylation of cyclohexene to cyclohexanecarboxaldehyde is significantly reduced when xenon is added to the reaction mixture at a concentration similar to that of the olefin. No significant effect is produced by helium or neon under similar conditions. These experiments suggest competitive coordination of xenon to the catalytically active cobalt species.

We have recently reported that appropriate concentrations of gases such as dinitrogen or argon produce a significant retarding effect on aldehyde formation in the cobalt-catalyzed hydroformylation of olefins.[1] This behavior has been ascribed to the ability of these additional substances to compete with dihydrogen and/or the olefin for the vacant coordination site on the catalytically active carbonylcobalt intermediate. If this interpretation is correct, the effect should depend on the availability of the outer-shell electrons of the donor, as measured by its first ionization potential (IP). As the first IP decreases on going from helium to xenon,[2][3] we would expect xenon to exhibit a higher coordination ability than the lighter rare gases, although its larger size could partly counteract this tendency.[4][5][6][7][8][9][10]

As a matter of fact, available literature data on adducts of rare gases with transition metals indicate a slightly higher coordinating ability of xenon compared to both argon and krypton.[11][12] A further relevant observation is that the bond dissociation energies (BDEs) for xenon with the pentacarbonylmetal(0) fragments of Group 6 do not show any marked dependence on the nature of the metal.[12]

With this background, we reckoned that, in extension of previous studies,[1] additional evidence for xenon coordination to a transition metal could be obtained by studying its effect on the cobalt-catalyzed hydroformylation reaction. Rate retardation would be expected if the presumably coordinatively unsaturated cobalt intermediate were to be intercepted by xenon rather than by dihydrogen and/or the olefin, thereby decreasing the steady-state concentration of the catalytically active species. The magnitude of any such effect would be difficult to predict, but some insight into this matter may be gained by considering the available thermodynamic data concerning metal−dihydrogen and metal−olefin bonds.

The tungsten−dihydrogen BDE has been estimated[13] to be 83 kJ mol^{-1} in $W(CO)_3(PR_3)_2(H_2)$, which is about 50 kJ mol^{-1} higher than that reported for the W−Xe bond in $W(CO)_5Xe$ (35.1 ± 0.8 kJ mol^{-1}[11]). If a similar difference in stability between dihydrogen and xenon is maintained under hydroformylation conditions, we may expect to see an effect on the product conversion. The manganese(I)−ligand (L) bond in $Mn(\eta^5\text{-}C_5H_5)(CO)_2L$ (L = *cis*-cyclooctene) has been estimated to require 102.4 ± 10 kJ mol^{-1} for dissociation.[14]

We report here the results of our investigation into the cobalt-catalyzed hydroformylation of cyclohexene in the presence of added xenon. Toluene was chosen as the reaction medium since competitive coordination of the catalytically active species by this solvent was anticipated to be minimized by both its self-aggregation (the relatively high enthalpy of vaporization[13g] is $\Delta H_v = 33.2$ kJ mol^{-1} at $T_{bp} = 383.6$ K) and owing to the disruption of resonance energy that would occur upon coordination through only part of the π electron density.

$$RCo(CO)_4 + L \rightleftarrows RCo(CO)_3L + CO$$

for	R = H, $Co(CO)_4$	L = H_2, olefin, Ar, Xe
for	R = alkyl, acyl	L = H_2, Ar, Xe

Our results are collected in Table 1, together with those from similar experiments (see Experimental Section) carried out in the presence of helium or neon. Helium and neon have no significant effect on the rate of the hydroformylation reaction; the slight decrease in conversion observed may be attributed to the dilution effect caused by the volume increase of the liquid medium due to the gas dissolution under the reaction conditions.

The presence of xenon has a negative effect on the rate of hydroformylation of the olefin. Taking into consideration that the experimentally determined amount of argon present in the liquid phase at 1000 bar and 373 K (0.086 mol) is, on a molar basis, approximately six times as large (see Experimental Section) as the amount of xenon (0.014 mol), the 30% drop in the conversion obtained in the presence of the latter suggests a stronger coordinating ability of xenon compared to argon, as anticipated in the introductory remarks and in agreement with the literature results.

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Table 1. Conversion (%) to cyclohexanecarboxyaldehyde in the hydroformylation of cyclohexene in the presence of rare gases (RG)[a]

RG	RG pressure				Ref.
	0 bar	500 bar	800 bar	1000 bar	
Helium[b]	30	29	27	–	[c]
Neon[b]	30	29	–	–	[c]
Argon[b]	30	19	10	9	[1]
	RG weight[b]				
	0 g	2.5 g	–	3.8 g	
Xenon[d]	30	25	–	21	[c]

[a] Reaction conditions: dry toluene, 7 mL; $Co_2(CO)_8$, 51 mg (0.149 mmol); cyclohexene, > 99.9% purity by GC, 504 mg (6.15 mmol); $p(CO) = 70 \pm 1$ bar (373 K); $p(H_2) = 85 \pm 2$ bar (373 K); autoclave volume, 25.4 mL; temperature, 373 K; reaction time, 3 h. – [b] Gases introduced in the following order: CO, dihydrogen, RG. – [c] This work. – [d] Gases introduced in the following order: CO (1 bar), xenon, CO (54 ± 2 bar at room temperature, 68 ± 2 bar at 373 K), H_2 (85 ± 3 bar at 373 K). Pressures are equilibrium readings after physical absorption (about 20 min).

Furthermore, in the presence of 270 bar of argon (19 mmol in the liquid phase) the conversion is not influenced, whereas in the presence the same molar amount of xenon in the liquid phase (18.5 bar, 19 mmol in the liquid phase) a reduction in the degree of conversion (16%) is observed.

In view of the BDE data mentioned above, a dihydrogen–xenon competition appears to be most likely. Catalytic hydrogenations represent another important class of reactions where indirect evidence concerning the coordinating ability of rare gases can be anticipated. Experiments along these lines, in both homogeneous and heterogeneous systems, will be undertaken in due course.

Experimental Section

The experiments in the presence of uncondensable gases (He or Ne) were carried out as follows: the catalyst, solvent, olefin, and carbon monoxide were introduced sequentially into the autoclave and the contents were heated at 373 K. Dihydrogen, followed by the additional rare gas, were then rapidly added. The reaction conditions were maintained for 3 h. In the case of xenon, which has a higher b.p. (162 K) than either helium or neon and is thus more easily condensed, the operations were carried out in the following sequence: introduction of the catalyst, solvent, olefin, xenon, and carbon monoxide at room temperature; heating to 373 K; pressurization with dihydrogen. The amount of xenon introduced was determined by the weight difference of the cylinder. At 373 K, the following equilibrium pressures (bar) were measured after introduction of xenon (weight of xenon in parentheses): 18.5 (2.5 g), 23.5 (3.8 g).

The amount of argon dissolved in the solution at 1015 bar and 373 K was experimentally determined to be about 0.086 mol; the amount of xenon (total 3.8 g) dissolved at the same temperature was estimated to be about 0.014 mol.

Acknowledgments

The authors wish to thank Prof. Fausto Calderazzo for very fruitful discussions and suggestions. This work has been partially supported by the Ministero della Università e della Ricerca Scientifica e Tecnologica (MURST).

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[1] F. Piacenti, F. Calderazzo, M. Bianchi, L. Rosi, P. Frediani, *Organometallics* **1997**, *16*, 4235.

[2] IP values (eV)[3]: He (24.587), Ne (21.564), Ar (15.760), Kr (14.000), Xe (12.130).

[3] *CRC Handbook of Chemistry and Physics* (Eds.: D. R. Lide, H. P. R. Frederikse), 77th ed., Boca Raton, New York, London, Tokyo, **1994–1995**, p. 10–205.

[4] The following van der Waals radii [Å] of rare gases have been reported[5][6][7]: He (1.40, 1.49, 1.79); Ne (1.54, 1.55, 1.6); Ar (1.88, 1.88, 1.92); Kr (2.02, 2.00, 1.98); Xe (2.16, 2.18, 2.18). Attempts have been made to calculate "covalent" bond lengths [Å] for rare gases and some typical values[8] are: He (0.4–0.6); Ne (0.6–0.7); Ar (0.94–0.95); Kr (1.00–1.18); Xe (1.30). An experimental determination of the covalent radius of xenon [1.543(1) Å] in Xe_2^+ (bond order 0.5) has recently been reported,[9] which is qualitatively in agreement with the covalent radius of iodine (1.357 Å) in solid I_2,[10] considering that the increase in effective nuclear charge and the decrease in bond order on going from iodine to xenon have opposing effects of unknown relative magnitudes.

[5] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

[6] R. Chauvin, *J. Phys. Chem.* **1992**, *96*, 9194.

[7] G. A. Cook, in *Argon, Helium and the Rare Gases* (Ed.: G. A. Cook), vol. 1, J. Wiley, New York, **1961**.

[8] J. E. Huheey, *J. Chem. Educ.* **1968**, *45*, 791, and references therein.

[9] T. Drews, K. Seppelt, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 273; *Angew. Chem.* **1997**, *109*, 264.

[10] F. van Bolhuis, P. B. Koster, T. Migchelsen, *Acta Crystallogr.* **1967**, *23*, 90.

[11] B. H. Weiller, *J. Am. Chem. Soc.* **1992**, *114*, 10910.

[12] J. R. Wells, E. Weitz, *J. Am. Chem. Soc.* **1992**, *114*, 2783.

[13] [13a] G. J. Kubas, *Acc. Chem. Res.* **1988**, *21*, 120. – [13b] R. H. Crabtree, *Acc. Chem. Res.* **1990**, *23*, 95. – [13c] D. M. Heinekey, W. J. Oldham, *Chem. Rev.* **1993**, *93*, 913. – [13d] D. M. Heinekey, T. A. Luther, *Inorg. Chem.* **1996**, *35*, 4396. – [13e] A. A. Gonzales, K. Zhang, S. P. Nolan, R. Lopez de la Vega, S. L. Mukerjee, C. D. Hoff, G. J. Kubas, *Organometallics* **1988**, *7*, 2429. – [13f] H. J. Wasserman, G. J. Kubas, R. R. Ryan, *J. Am. Chem. Soc.* **1986**, *108*, 2294. – [13g] See ref.[3], p. 6–110.

[14] J.-K. Klassen, M. Selke, A. A. Sorensen, G. K. Yang, *J. Am. Chem. Soc.* **1990**, *112*, 1267.

Received July 10, 1998
[I98231]