# Photochemical Hydroformylation of Olefins with Cobalt Catalysts. 1. Neutral Cobalt Carbonyls

**Manfred J. Mirbach,* Marlis F. Mirbach, Alfons Saus, Nikolaos Topalsavoglou, and Tuyet Nhu Phu**

*Contribution from the Universität Duisburg, GH, Fachbereich 6, Angewandte Chemie, D-4100 Duisburg 1, West Germany.*

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**Abstract:** The $Co_2(CO)_8$ and $Co_4(CO)_{12}$ catalyzed hydroformylation of octene-1 and cyclohexene in hydrocarbon solvents is strongly retarded by UV irradiation. In situ UV and IR spectroscopy reveals that the active catalyst $HCo(CO)_4$ is decomposed via photochemically produced $\cdot Co(CO)_4$ radicals. Neither in the presence of carbon monoxide and hydrogen nor upon addition of $HSi(OEt)_3$ does irradiation of $Co_2(CO)_6(P(n\text{-}Bu)_3)_2$ lead to the formation of $HCo(CO)_3P(n\text{-}Bu)_3$. Added octene-1 is isomerized to internal olefins under these conditions, but not hydroformylated. Seventeen-electron species of the type $\cdot Co(CO)_3L$ ($L$ = CO or $P(n\text{-}Bu)_3$), produced by photolytic cleavage of the corresponding dimers, are obviously not able to activate molecular hydrogen or carbon monoxide nor to abstract hydrogen from methylcyclohexane or triethoxysilane.

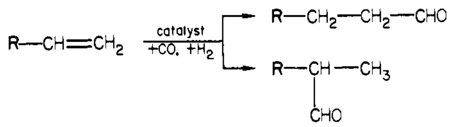
An increasing number of publications show that there is a substantial interest in the application of photochemical techniques to homogeneous catalysis. The activation of hydrogen and carbon monoxide by transition-metal carbonyls is particularly important. It has been demonstrated that dinuclear carbonyl complexes, like dicobalt octacarbonyl (a very important hydroformylation catalyst), form mononuclear species under UV irradiation (eq 1).[1]

$$Co_2(CO)_6L_2 \underset{}{\overset{h\nu}{\rightleftharpoons}} 2\dot{C}o(CO)_3L \qquad (1)$$

$$L = \text{CO, phosphine}$$

The mononuclear 17 electron species produced are usually very reactive, and it has been proposed to use the photochemical activation of transition-metal carbonyls to produce active catalytic intermediates (e.g., hydridocomplexes).[2] It remains, however, to be demonstrated that 17 electron metal carbonyl species are indeed useful catalyst precursors in a hydroformylation reaction (eq 3).[3]

$$\cdot Co(CO)_3L \xrightarrow[-CO]{} \cdot Co(CO)_2L \xrightarrow[?]{+H_2} HCo(CO)_2L \qquad (2)$$



(3)

Well-known examples which show that light can initiate and accelerate catalytic reactions include the photocatalyzed olefin isomerization, hydrogenation, hydrosilylation, oligomerization, and metathesis.[4] It is most likely, however, that these examples proceed in the classical way via a sequence of 18 and 16 electron species. To extent these examples to the photocatalyzed hydroformylation reaction, we studied the photochemistry of cobalt carbonyls in the presence of high synthesis gas pressure both with and without added olefins. In this paper we describe the results obtained with $Co_2(CO)_8$, $Co_4(CO)_{12}$, and $Co_2(CO)_6(P(n\text{-}Bu)_3)_2$ in hydrocarbon solvents, using an experimental technique which allows photochemical reactions to be run at high pressure and monitored simultaneously by GLC and IR and UV spectroscopy.[5]

## Experimental Section

**Photochemical Experiments at Elevated Pressure.** Preparative runs were performed in a 1 L UV autoclave equipped either with a medium-pressure mercury lamp (500 to 700 W, Quarzlampen GmbH, Hanau) and a Pyrex filter or with a low-pressure mercury lamp (TNN 15/32, Quarzlampen GmbH, Hanau) and a quartz filter. Vigorous mixing of the gas and liquid phases was achieved by means of a magnetically driven up-and-down stirrer (Figure 1).[6]

In a typical run the autoclave was flushed with argon, 600 mL of starting solution were introduced, and the autoclave was closed, flushed with 20 bar of synthesis gas (or other gas), and pressurized with synthesis gas ($CO/H_2 = 1$) to a desired value. The irradiation was started after the system had been thermostated to the desired temperature. Samples of the gaseous and the liquid phases could be taken via metering valves for analysis by GLC.

In order to monitor the reaction by IR and UV spectroscopy the UV autoclave was connected to a high-pressure system consisting of a piston pump, a UV cell with quartz windows in a Cary 118 UV/VIS spectrometer, an IR cell with $CaF_2$ windows in a Zeiss IMR-25 IR spectrometer, and an outlet for GLC analysis. The reaction solution was pumped through the system and spectra were recorded at the desired time intervals. The IR cell was kept at the same temperature as the autoclave, whereas the UV spectra were recorded at room temperature. The optical path length of the home-built cells was approximately 0.5 mm and the time required to fill the whole system with solution was 1 to 3 min, depending on the pumping speed.

**Preparation and Identification of Catalysts.** $Co_2(CO)_8$ was prepared from cobalt acetate[7] and was characterized by its IR absorption[8] at 2068, 2041, 2024 (terminal CO's) and 1866, 1857 cm$^{-1}$ (bridging CO's) and its UV absorption[9] at 350 and 275 nm.

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(1) (a) Sweany, R. L.; Brown, T. L. *Inorg. Chem.* **1977**, *16*, 421. (b) Reichel, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 6769.

(2) The enhanced reactivity of 17-electron transition-metal carbonyls has been shown for a number of metals. For example, see: (a) Kochi, J. K. "Organometallic Mechanisms and Catalysts"; Academic Press: New York, 1978. (b) Absi-Halabi, M.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2982. (c) Krusic, P. J.; San Filippo, J., Jr.; Hutchinson, B.; Hance, R. L.; Daniels, L. M. *Ibid.* **1981**, *103*, 2129. Krusic, P. *Ibid.* **1981**, *103*, 2131.

(3) For reviews about the hydroformylation reaction see: (a) Paulik, F. E. *Catal. Rev.* **1972**, *6*, 49. (b) Falbe, J. "Carbon Monoxide in Organic Synthesis"; Springer Verlag: Berlin-Heidelberg-New York, 1970. (c) Parshall, G. W. *J. Mol. Catal.* **1978**, *4*, 243.

(4) (a) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979. (b) Wrighton, M. S. *Chem. Rev.* **1974**, *74*, 401. (c) Hennig, H.; Thomas, P.; Wagener, R.; Rehorek, D.; Jurdeczka, K. *Z. Chem.* **1977**, *17*, 241.

(5) For preliminary reports of parts of the results presented in this paper see: (a) Mirbach, M. J.; Phu, T. N.; Topalsavoglou, N.; Mirbach, M. F.; Saus, A. IUPAC-Symposium on Photochemistry, VIII, Seefeld, Austria, 1980; Contributed Paper No. 116. (b) Mirbach, M. J.; Phu, T. N.; Topalsavoglou, N.; Saus, A. 2nd International Symposium on Homogeneous Catalysis, Düsseldorf (F.R. Germany), 1980, Abstracts of Papers p 70. (c) Mirbach, M. J.; Mirbach, M. F.; Topalsavoglou, N.; Phu, T. N.; Saus, A. *Angew. Chem.*, **1981**, *93*, 391; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 381.

(6) Instrumental details are described in: (a) Saus, A. *CZ-Chem.-Tech.* **1975**, *2*, 19. (b) Mirbach, M. J. Thesis, RWTH Aachen, 1976; Mirbach, M. F. Thesis, RWTH Aachen, 1976; Gascard, T. Thesis, RWTH Aachen, 1977.

(7) Szabo, P.; Marko, L.; Bor, G. *Chem. Technol.* **1961**, *13*, 549.

(8) Friedel, R. A.; Wender, I.; Shufler, S. L.; Sternberg, H. W. *J. Am. Chem. Soc.* **1955**, *77*, 3951.

(9) Abrahamson, H. B.; Frazier, C. C.; Ginley, D. S.; Gray, H. B.; Lilienthal, J.; Taylor, D. R.; Wrighton, M. S. *Inorg. Chem.* **1977**, *16*, 1554.

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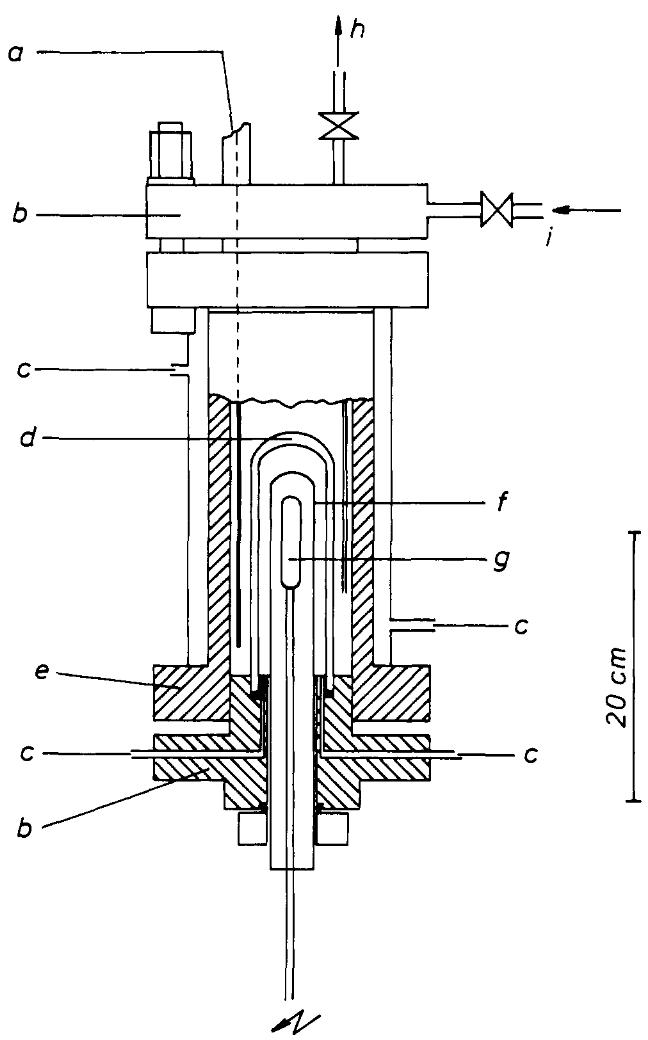

**Figure 1.** Schematic drawing of the UV autoclave: (a) Magnetic stirrer, (b) flanged lid, (c) connection for thermostat, (d) pressure stable quartz cyclinder, (e) Teflon packing, (f) Pyrex tube, (g) medium-pressure Hg lamp, (h) sampling valve, connection to high-pressure UV and IR cells, (i) entrance valve (from UV and IR cell).

$HCo(CO)_4$ was formed from $Co_2(CO)_8$ under hydrogen pressure. It was characterized by its IR absorption at 2053 and 2030 $cm^{-1}$ and its characteristic UV absorption band at 230 nm.[10]

$Co_2(CO)_6(P(n\text{-}Bu)_3)_2$ was prepared from $Co_2(CO)_8$ and tri-*n*-butylphosphine. IR 1953 $cm^{-1}$; UV 365 nm.[11]

$HCo(CO)_3P(n\text{-}Bu)_3$ was formed during the irradiation of $[Co(CO)_3(P(n\text{-}Bu)_3)_2][Co(CO)_4]$ under $CO/H_2$ pressure.[12] IR 1970 $cm^{-1}$; UV, the rather low concentrations present in our experiments did not show a significant UV absorption although a green-yellow color of the neat compound is reported.[13]

$[Co(CO)_3(P(n\text{-}Bu)_3)_2][Co(CO)_4]$ is formed as a yellow precipitate when phosphine is added to a hydrocarbon solution of $Co_2(CO)_8$.[11] IR (methanol) 1985, 1995 for the cation and 1910 $cm^{-1}$ for the anion. IR (acetone) 1990–2000 (cation) and 1885 $cm^{-1}$ (anion).[14] UV (methanol) 245 nm (cation). There was no characteristic UV absorption of the anion.[12]

$Co_4(CO)_{12}$ was prepared from $Co_2(CO)_8$[8] and identified by its IR absorption at 1864 $cm^{-1}$.[15]

**Other Chemicals.** All other chemicals were commercial products and were used without further treatment. It was found that further purification did not influence the reactions.

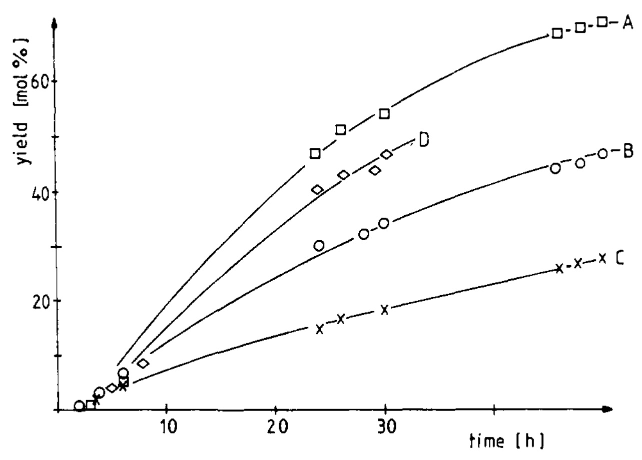

**Figure 2.** Hydroformylation of octene-1 with $Co_2(CO)_8$ in methylcyclohexane: (A) thermal, (B) irradiation with a 500 W lamp, (C) irridation with a 700 W lamp, (D) irradiation with a low-pressure Hg lamp (TNN 15/32). Reaction conditions: 75 °C, 75 bar $CO/H_2 = 1/1$, 17 mmol/L $Co_2(CO)_8$, 1.6 M octene-1 in 430 mL of methylcyclohexane; lamp in B and C, medium-pressure Hg lamp TQ718, Quarzlampen GmbH Hanau.

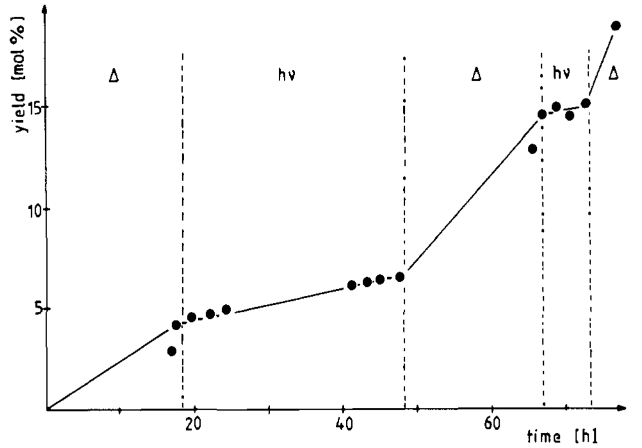

**Figure 3.** Hydroformylation of cyclohexene with $Co_2(CO)_8$ and alternating irradiation and dark periods. Reaction conditions: 2.9 mmol/L $Co_2(CO)_8$, 2.8 M cyclohexene in 490 mL of methylcyclohexane, 80 °C, 85 bar $CO/H_2 = 1/1$.

**Product Analysis.** Organic products were analyzed by GLC on a Carlo Erba CE 2150 instrument with a flame ionization detector, using a UCON LB 550x and a UCON HB 5100 glass capillary column (100 m × 0.25 mm) with nitrogen as the carrier gas.

The cobalt carbonyls were determined by IR and UV spectroscopy. Because of the uncertain extinction coefficients only relative yields are given.

In our experiments the catalyst concentration and the synthesis gas pressure are practically constant at low conversions and do not change more than 10% when the olefin is completely converted.

## Results

**$Co_2(CO)_8$.** With dicobalt octacarbonyl as the starting catalyst and methylcyclohexane as the solvent octene-1 is slowly hydroformylated at a $CO/H_2$ pressure of 75 bar and at 75 °C (Figure 2). After 50 h ~80% of the olefin is converted to products. Besides the expected aldehyde (normal to branched ratio n/i = 4) small amounts of $C_9$-alcohols and the corresponding formates (~1%) are formed. Isomerization and hydrogenation of the olefin is negligible. Under completely analogous conditions but with additional irradiation by a medium-pressure mercury lamp through Pyrex the aldehyde formation rate decreases significantly (Figure 2). The aldehyde yield after 50 h drops to 47% when a 500 W lamp is used and to 28% when a 700 W lamp is used. The n/i ratio and the product distribution of the side reactions are not significantly affected by UV irradiation.

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[11] Manning, A. R. *J. Chem. Soc.* **1968**, 1135.

[12] Mirbach, M. J.; Mirbach, M. F.; Saus, A.; Topalsavoglou, N.; Phu, T. N. *J. Am. Chem. Soc.*, following paper in this issue.

[13] Pregaglia, G. F.; Andreetta, A.; Ferrari, G. F.; Ugo, R. *J. Organomet. Chem.* **1971**, *30*, 387.

[14] Pregaglia, G. F.; Andreetta, A.; Gregorio, G.; Ferrari, G. F.; Montrasi, G.; Ugo, R. *Chim. Ind. (Milan)* **1972**, *55*, 203.

[15] Bor, G.; Dietler, U. K.; Pino, P.; Poe, A. *J. Organomet. Chem.* **1978**, *162*, 189.

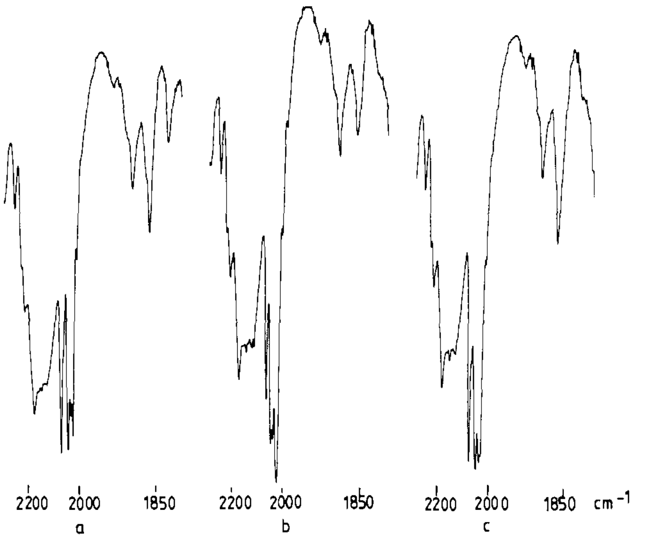

**Figure 4.** IR absorption of $Co_2(CO)_8/HCo(CO)_4$ mixtures at 80 °C and 85 bar $CO/H_2$ pressure: (a) after 1 h, (b) after 69 h, (c) after 78 h. Reaction conditions: 17 mmol of $Co_2(CO)_8$ in 600 mL of methylcyclohexane, 80 °C, 85 bar $CO/H_2$ = 1/1.

Similar results are obtained when a low-pressure mercury lamp is used for irradiation (Figure 2). In this case the total yield after 30 h reaction time drops from 55% under thermal conditions to 48% under photochemical conditions. In addition to the aldehyde small amounts (<2%) of the corresponding alcohols and their formic acid esters are formed. The mass balance of all identified products shows that no condensation products are formed. Thus the lower yields in the photochemical experiments are not due to any side reactions of the aldehydes.

The observed reduction of the hydroformylation rate due to UV irradiation is not limited to straight-chain normal olefins. Figure 3 shows that the formation of cyclohexane aldehyde from cyclohexene at 80 °C and 85 bar $CO/H_2$ pressure is strongly inhibited when the reaction solution is irradiated. In an experiment where irradiation and dark periods alternate it is striking that product is only formed during the dark periods (Figure 3).

Simultaneous observation of the UV and IR spectra during the hydroformylation of cyclohexene showed absorption bands of $Co_2(CO)_8$ only. There was not significant change in the spectra during the course of the reaction.

During both the irradiation and dark periods no evidence of $HCo(CO)_4$ was obtained under these conditions. This was probably because the cobalt carbonyl hydride and the olefin react so fast that the $HCo(CO)_4$ cannot be detected by our experimental method.[16]

In order to find out more about the catalytic intermediates the UV and IR absorption spectra were monitored under hydroformylation conditions, but in the absence of olefin. Under these conditions the alternating thermal and irradiation periods are accompanied by changes in the spectra. In the dark periods $HCo(CO)_4$ builds up. This is indicated by an increasing intensity of the IR bands at 2032 and 2055 cm⁻¹ (for representative spectra see Figure 4). Simultaneously the UV absorption of $Co_2(CO)_8$ at 350 nm decreases and a shoulder appears at 230 nm (due to $HCo(CO)_4$[17]) (see Figure 6). Figure 6).

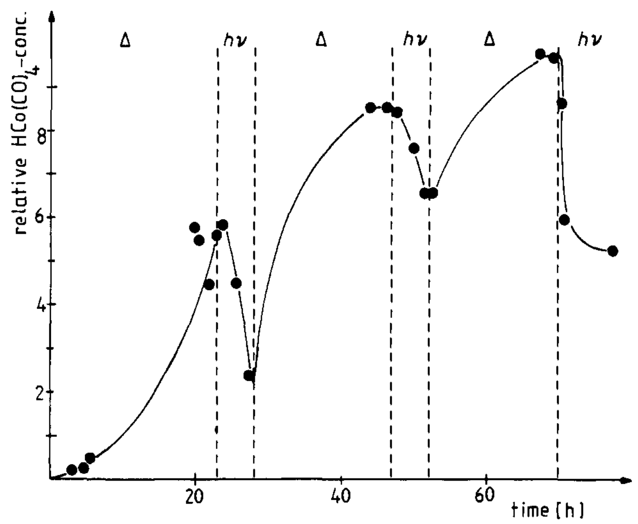

**Figure 5.** Relative intensities of the IR absorption band at 2032 cm⁻¹, assigned to $HCo(CO)_4$. Reaction conditions: 17 mmol of $Co_2(CO)_8$ in 600 mL of methylcyclohexane, 80 °C, 85 bar $CO/H_2$ = 1/1.

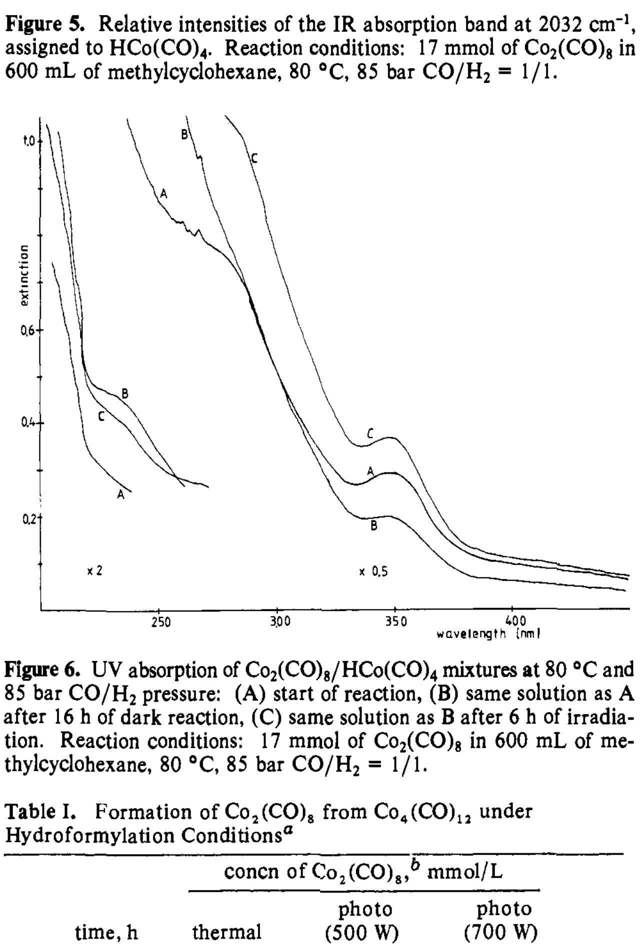

**Figure 6.** UV absorption of $Co_2(CO)_8/HCo(CO)_4$ mixtures at 80 °C and 85 bar $CO/H_2$ pressure: (A) start of reaction, (B) same solution as A after 16 h of dark reaction, (C) same solution as B after 6 h of irradiation. Reaction conditions: 17 mmol of $Co_2(CO)_8$ in 600 mL of methylcyclohexane, 80 °C, 85 bar $CO/H_2$ = 1/1.

Table I. Formation of $Co_2(CO)_8$ from $Co_4(CO)_{12}$ under Hydroformylation Conditions[a]

| | concn of $Co_2(CO)_8$,[b] mmol/L | | |
|---|---|---|---|
| time, h | thermal | photo (500 W) | photo (700 W) |
| 0 | 0 | 0 | 0 |
| 2 | 10.8 | 8.5 | 10.3 |
| 4 | 12.6 | 12.4 | 14.4 |
| 6 | 14.0 | 14.6 | 16.6 |
| 8 | 15.0 | 15.7 | 17.0 |

[a] Conditions: 8.5 mmol/L of $Co_4(CO)_{12}$, 1.6 M octene-1 in 430 mL of methylcyclohexane, 75 °C, 75 bar $CO/H_2$ = 1/1, 500 or 700 W medium-pressure Hg lamp through Pyrex. [b] Measured by IR spectroscopy as described in ref 15.

When the light is turned on, the IR bands of $HCo(CO)_4$ diminish and the bands of the terminal CO's of $Co_2(CO)_8$ increase (Figure 4c). Also, the UV absorption band at 350 nm increases and the shoulder at 230 nm disappears again (Figure 6). Figure 5 shows the relative intensities of the IR band at 2032 cm⁻¹ during dark and irradiation periods, which are proportional to the concentration of $HCo(CO)_4$.

Finally a known amount of cyclohexanal was introduced into the reaction mixture which contained $HCo(CO)_4$ and $Co_2(CO)_8$.

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[16] In our experimental system it takes about 30 to 60 s for the solution to reach the IR cell through a capillary tube. During this time no mixing between gas and liquid phases takes place. Therefore it may be that our spectra are not representative of the equilibrium mixture in the autoclave. This is, however, irrelevant for the further discussion, since we are not considering these equilibria quantitatively. The experiment without added olefins overcomes this practical problem. Similar problems are discussed in: Alemdaroglu, N.; Penninger, J. N. L.; Oltay, E. *Monatsh. Chem.* **1976**, 107, 1153. Whyman, R. *J. Organomet. Chem.* **1974**, *81*, 97.

[17] Christahl, M.; Saus, A. *Z. Naturforsch., B* **1977**, *32B*, 637.

The same changes in the UV and IR spectra occur upon irradiation, as described before. The aldehyde concentration remained constant during 24 h of alternating dark and irradiation periods.

**$Co_4(CO)_{12}$.** When tetracobalt dodecacarbonyl is used as starting catalyst, the effect of UV irradiation is the same as that described for $Co_2(CO)_8$, i.e., with this catalyst the hydroformylation reaction is also inhibited by UV light.[18] The tetranuclear complex is converted to $Co_2(CO)_8$ during the reaction but, in contrast to similar experiments with CO at normal pressure,[19] this conversion is only insignificantly enhanced by irradiation (Table I).

It should also be mentioned that all the described irradiation effects are qualitatively independent of temperature and synthesis gas pressure. However, the absolute rates are, of course, increased with increasing temperature and pressure.[20]

**$Co_2(CO)_8$ + Phosphine.** The hydroformylation reaction of octene-1 at 80 °C and 75 bar $CO/H_2$ pressure was repeated with a tenfold excess of tri-*n*-butylphosphine to dicobalt octacarbonyl. Again the reaction was followed by IR and UV spectroscopy during alternating irradiation and dark periods. Immediately after the addition of phosphine to the solution the yellow ionic complex **1** is formed, which is insoluble in methylcyclohexane. The first spectrum after heating the solution to 75 °C already shows the presence of $Co_2(CO)_6(P(n\text{-}Bu)_3)_2$ (**2**), indicated by the UV band at 365 nm and the IR bands at 1971, 1952, 1927 cm$^{-1}$. These absorptions increase with time independently of whether the solution is irradiated or not, since the insoluble complex **1** is slowly converted to the soluble carbonyl **2**.

$$Co_2(CO)_8 + 2P(n\text{-}Bu)_3 \rightarrow \underset{\mathbf{1}}{[Co(CO)_3(P(n\text{-}Bu)_3)_2][Co(CO)_4]} + CO \quad (4)$$

$$\mathbf{1} \rightarrow \underset{\mathbf{2}}{Co_2(CO)_6(P(n\text{-}Bu)_3)_2} + CO \quad (5)$$

No hydroformylation or other reactions are observed even after a reaction time of 30 h and no evidence of any change in complex **2** is obtained. In particular, no $HCo(CO)_3P(n\text{-}Bu)_3$ can be detected.

When 30% of triethoxysilane is added to the reaction mixture containing **1** and phosphine and this solution is irradiated under hydroformylation conditions, a double bond migration of the octene is observed, but no oxo product is formed. The corresponding control experiment without irradiation did not show the migration of the double bond and also did not result in any oxo product. This experiment is similar to the one performed by Reichel and Wrighton, who irradiated the carbonyl complex **2** in a mixture of pentene-1 and a trialkylsilane in an argon atmosphere and observed a rather rapid double bond migration of the olefin, which also did not occur in their control experiments.[1b]

## Discussion

**$Co_2(CO)_8$.** It is generally agreed that $HCo(CO)_4$ and $HCo(CO)_3$ are the key intermediates in the hydroformylation reaction (eq 3).[3,21] The expectation that the formation of these species from neutral carbonyl precursors via a reaction with molecular hydrogen would be enhanced by UV irradiation is *not* fullfilled. On the contrary, the rates of hydroformylation and $HCo(CO)_4$ formation from $Co_2(CO)_8$ in hydrocarbon solvents are slowed down when the reaction mixture is irradiated with UV light. Figure 5 shows that the cobalt carbonyl hydride is even destroyed under the conditions employed (i.e., irradiation with a medium-pressure mercury lamp through Pyrex). $HCo(CO)_4$ does not significantly absorb above 300 nm.[10,17] Thus nearly all of the light is absorbed by $Co_2(CO)_8$, which is reported to undergo homolytic cleavage of the cobalt–cobalt bond to the 17 electron species $\cdot Co(CO)_4$.[1a,22]

$$Co_2(CO)_8 \overset{h\nu}{\rightleftharpoons} 2\dot{C}o(CO)_4 \quad (6)$$

Simultaneously $HCo(CO)_4$ is formed by a thermal reaction of $Co_2(CO)_8$ and hydrogen:

$$Co_2(CO)_8 + H_2 \overset{\Delta}{\rightleftharpoons} 2HCo(CO)_4 \quad (7)$$

Wegman and Brown[22] have proposed a mechanism which explains the decomposition of $HCo(CO)_4$ via a chain reaction with $\cdot Co(CO)_4$ as the chain carrier (eq 8 to 12). The final decomposition product is $Co_2(CO)_8$.

$$\cdot Co(CO)_4 \rightarrow \cdot Co(CO)_3 + CO \quad (8)$$

$$\cdot Co(CO)_3 + HCo(CO)_4 \rightarrow \cdot HCo_2(CO)_7 \quad (9)$$

$$\cdot HCo_2(CO)_7 + HCo(CO)_4 \rightarrow H_2Co_2(CO)_7 + \cdot Co(CO)_4 \quad (10)$$

$$H_2Co_2(CO)_7 \rightarrow H_2 + Co_2(CO)_7 \quad (11)$$

$$Co_2(CO)_7 + CO \rightarrow Co_2(CO)_8 \quad (12)$$

Our experiments are in complete agreement with this mechanism. It must be concluded that the photochemically produced radical $\cdot Co(CO)_4$ does *not* react with molecular hydrogen to give cobalt carbonyl hydride (eq 13) under the employed reaction conditions. Rather $HCo(CO)_4$ is only formed in a thermal reaction directly from $Co_2(CO)_8$ (eq 7).

$$\cdot Co(CO)_4 + H_2 \nrightarrow HCo(CO)_4 \quad (13)$$

Light absorption by $HCo(CO)_4$ is not considered to be important in this context for two reasons: (i) $HCo(CO)_4$ has no significant absorption above 300 nm and it was shown that irradiation with light of wavelengths shorter than 310 nm is required to produce $HCo(CO)_3$.[23,24] (ii) In the presence of olefin $HCo(CO)_4$ reacts rather rapidly with the double bond and thus its stationary concentration remains low during the course of the reaction. This is indicated by the lack of $HCo(CO)_4$ absorption bands in the IR spectra.

**$Co_2(CO)_8$ + $P(n\text{-}Bu)_3$.** A large excess of tri-*n*-butylphosphine slows down the thermal hydroformylation reaction, and under the mild conditions used in our experiments no products are formed when methylcyclohexane is used as the solvent. Additional UV irradiation does not lead to any activation of the catalyst. The only transition-metal complex present in the reaction solution is $Co_2(CO)_6(P(n\text{-}Bu)_{32}$ (**2**), as indicated by the IR and UV spectra. Similar observations were made when the complex **2**, prepared separately, was used as the starting catalyst.

Complex **2** is believed[1b] to form the 17 electron species **3** photochemically (eq 14). According to our experiments **3** is unable to react with molecular hydrogen to give **4** or to initiate the hydroformylation reaction (eq 15). When $HCo(CO)_3P(n\text{-}Bu)_3$ (**4**) was produced by a different route it was shown to be an active catalyst for the oxo reaction.[12]

$$\underset{\mathbf{2}}{Co_2(CO)_6(P(n\text{-}Bu)_3)_2} \overset{h\nu}{\rightleftharpoons} \underset{\mathbf{3}}{2\dot{C}o(CO)_3P(n\text{-}Bu)_3} \quad (14)$$

$$\mathbf{3} + H_2 \nrightarrow \underset{\mathbf{4}}{HCo(CO)_3P(n\text{-}Bu)_3} \quad (15)$$

It was proposed that the paramagnetic species **3** reacts with silane, $HSiR_3$, to give the hydride complex **4**, the evidence for its formation being the observed double bond migration of pentene.[1b] Under the conditions of our photochemical experiments (80 °C, 80 bar $CO/H_2$), addition of silane causes a similar double bond migration of octene, but does *not* lead to the hydroformylation

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[18] The thermal reaction rates are higher with $Co_4(CO)_{12}$ than with $Co_2(CO)_8$ as the starting catalyst, due to faster formation of $HCo(CO)_3$ from the tetranuclear carbonyl. This "cluster effect" has been described previously; Lennertz, A. M.; Laege, J.; Mirbach, M. J.; Saus, A. *J. Organomet. Chem.* **1979**, *171*, 203.

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[21] (a) Breslow, D. S.; Heck, R. F. *Chem. Ind.* (*London*) **1960**, 467. (b) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1961**, *83*, 1097. (c) Wender, I.; Sternberg, H. W.; Orchin, M. *J. Am. Chem. Soc.* **1961**, *83*, 4023.

[22] Wegman, R. W.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 2494.

[23] Wermer, P.; Ault, B. S.; Orchin, M. *J. Organomet. Chem.* **1978**, *162*, 189. Sweany, R. L. *Inorg. Chem.* **1980**, *19*, 3572.

[24] In most of the experiments described here Pyrex-filtered light from a medium-pressure mercury lamp was used, which has almost no emission intensity below 300 nm.

reaction. We therefore must conclude either that the formed hydride **4** is unable to catalyze the oxo reaction, or that another species is formed which is able to catalyze the double bond migration but not the hydroformylation reaction. The latter alternative seems to us the more likely.[25]

## Conclusion

It is expected that UV irradiation of dinuclear cobalt carbonyls produces paramagnetic "reactive" 17 electron species. In fact these species do not seem to be precursors of the hydroformylation catalysts nor do they seem to activate molecular hydrogen or molecular carbon monoxide at synthesis gas pressures up to 85 bar and temperatures up to 85 °C. Thus, it is likely that the intermediates, which are produced photochemically, recombine too fast to allow the macroscopic observation of reactions with CO or $H_2$.

**Acknowledgment.** We would like to thank Dr. Paul Krusic, Du Pont de Nemours, Wilmington, who is independently working on similar problems, for interesting discussions and for making available to us some of his unpublished results.

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[25] It has been suggested by one of the referees that the key step in Reichel and Wrighton's mechanism for the formation of $HCo(CO)_3L$, namely the formation of a 15-electron species, is inhibited in the presence of a high CO pressure

$$\cdot Co(CO)_3L \rightleftharpoons \cdot Co(CO)_2L + CO$$

However, since we do observe isomerization under 80 bar $CO/H_2$ pressure, a different catalytic species must be responsible for the isomerization. A possible candidate is $R_3SiCo(CO)_3$ as discussed by: Reichel, C. L.; Wrighton, M. S. *Inorg. Chem.* **1980**, *19*, 3858.

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# Photochemical Hydroformylation of Olefins with Cobalt Catalysts. 2. Ionic Cobalt Carbonyls

**Manfred J. Mirbach,* Marlis F. Mirbach, Alfons Saus, Nikolaos Topalsavoglou, and Tuyet Nhu Phu**

*Contribution from the Universität Duisburg, GH, Fachbereich 6, Angewandte Chemie, D-4100 Duisburg 1, West Germany.*

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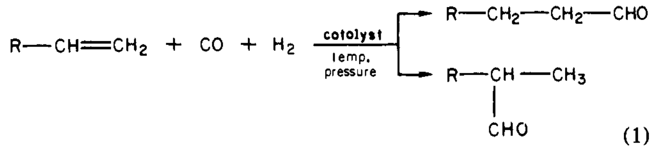
**Abstract:** In the presence of $CO/H_2$ or CO, $H_2$, and $P(n\text{-}Bu)_3$ a methanol solution of cobalt acetate is photochemically reduced to low-valent cobalt carbonyls, which are active catalysts for the hydroformylation of olefins. The hydroformylation of cyclohexene with $Co_2(CO)_8$ in methanol is enhanced by UV irradiation, probably via activation of the tetracarbonyl cobaltate ion (**2**) which is formed during the reaction. Similarly in the presence of excess phosphine the $[Co(CO)_3(P(n\text{-}Bu)_3)_2][Co(CO)_4]$ complex ([**1**][**2**]), which at 80 °C and 80 bar synthesis gas pressure is completely inactive toward hydroformylation, is photochemically converted to $HCo(CO)_3P(n\text{-}Bu)_3$ (**4**). **4** is a very selective catalyst for the formation of *n*-aldehydes from α-olefins. Linear oxo products (99% and 90%) are obtained from propene and octene-1, respectively. In situ IR and UV spectroscopy shows that **4** is mainly produced by photolysis of the cation **1**, and to a lesser extend via photolysis of **2**.

The catalytic hydroformylation (or oxo-reaction) of olefins to aldehydes and alcohols is an outstanding example of a homogeneously catalyzed reaction which is of great commercial importance. Since its discovery by Otto Roelen in Germany in 1937 the reaction has been the subject of innumerable publications and patents.[1]



$$R{-}CH{=}CH_2 + CO + H_2 \xrightarrow[\text{temp., pressure}]{\text{cotolyst}} \begin{cases} R{-}CH_2{-}CH_2{-}CHO \\ R{-}CH(CHO){-}CH_3 \end{cases} \quad (1)$$

Cobalt or rhodium carbonyls are commonly used as catalysts. Addition of trialkylphosphines to the cobalt catalyst increases its selectivity toward the more valuable straight-chain products, but relatively high temperatures (150–180 °C) are required to activate the phosphine-modified catalyst. Further developments of this process are directed toward milder reaction conditions and higher selectivities toward the desired *n*-aldehydes or *n*-alcohols.[2]

It is often suggested in the literature that light may be applied to activate homogeneous catalysts. This should allow catalytic processes to be run at lower temperatures and also the conversion of thermally labile molecules (e.g., in a hydroformylation reaction). It has been shown, however, that irradiation of neutral cobalt carbonyls under hydroformylation conditions does *not* lead to higher reaction rates. On the contrary the active catalytic species $HCo(CO)_3L$ (L = CO or $P(n\text{-}Bu)_3$) may even be destroyed photochemically.[3]

In this paper we report that the chemistry is considerably different when ionic cobalt compounds in polar solvents (e.g., methanol) are used as photocatalysts, and that it is indeed possible to hydroformylate olefins photochemically under very mild thermal conditions and with high selectivities toward the desired straight-chain products.[4] The mechanisms of the reactions were investigated by high-pressure IR and UV spectroscopy.

## Experimental Section

$Co(OAc)_2{\cdot}4H_2O$ (Merck), $P(n\text{-}Bu)_3$ (EGA-Chemie), octene-1 (EGA-Chemie), propene (Messer-Griesheim), and methanol were used without

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[1] For reviews on hydroformylation see: (a) Parshall, G. W. *J. Mol. Catal.* **1978**, *4*, 243. (b) Falbe, J.; Payer W. In "Ullmann Enzyklopaedie der Technischen Chemie"; Urban & Schwarzenberg: München, 1974; Vol. 7, p 118. (c) Paulik, F. E. *Catal. Rev.* **1972**, *6*, 49. (d) Falbe, J. "Carbon Monoxide in Organic Synthesis"; Springer: Berlin-Heidelberg-New York, 1970.

[2] (a) Pruett, R. L.; Smith, J. A. U.S. Patent 3 917 661, 1975. (b) Cornils, B.; Payer, R.; Traenckner, K. C. *Hydrocarbon Process.* **1975**, 83. (c) Siegel, H.; Himmele, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 178.

[3] Mirbach, M. J.; Mirbach, M. F.; Saus, A.; Topalsavoglou, N.; Phu, T. N. *J. Am. Chem. Soc.*, preceding paper in this issue.

[4] The qualitative aspects of these experiments were discussed in preliminary accounts: (a) Mirbach, M. J.; Phu, T. N.; Topalsavoglou, N.; Mirbach, M. F.; Saus, A. IUPAC Symposium on Photochemistry, VIII, Seefeld, Austria 1980, Contributed Paper No. 116, (b) Mirbach, M. J.; Phu, T. N.; Topalsavoglou, N.; Saus A. 2nd International Symposium on Homogeneous Catalysis, Düsseldorf, F.R. Germany, 1980; Abstracts of Papers p 70, (c) Mirbach, M. J.; Mirbach, M. F.; Topalsavoglou, N.; Phu, T. N.; Saus, A. *Angew. Chem.* **1981**, 93, 391; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 381.