Journal of Organometallic Chemistry, 191 (1980) 295—302

FUNDAMENTAL METAL CARBONYL EQUILIBRIA: A QUANTITATIVE INFRARED SPECTROSCOPIC STUDY OF THE EQUILIBRIUM BETWEEN DICOBALT OCTACARBONYL AND TETRACOBALT DODECACARBONYL UNDER CARBON MONOXIDE PRESSURE IN HEXANE SOLUTION *

GYŐRGY BOR und URS K. DIETLER

Department of Industrial and Engineering Chemistry, Swiss Federal Institute of Technology (E.T.H.) CH-8092 Zurich (Switzerland)

(Received October 15th, 1979)

Summary

The equilibrium between $Co_2(CO)_8$ and $Co_4(CO)_{12}$ has been investigated in hexane solution in the temperature range 105—145°C under carbon monoxide pressure (6—14 bar). The data obtained by infrared analytical monitoring of the system in a high-pressure cell allow a reasonably precise extension of the calculated equilibrium concentration between —20 and 300°C. The thermodynamic parameters obtained for this system are: ΔH^0 29.5 ± 0.5 kcal mol^{-1}, ΔS^0 135 ± 3 cal mol^{-1} K^{-1}. The stability regions of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ in terms of p(CO) and temperature are discussed.

It has been emphasized recently, that the existence of metal carbonyl clusters "must be connected either with a delicate thermodynamic balance or with remarkably high activation energies" [1]. However, quantitative data about the characteristics of the formation or degradation reactions of metal carbonyl clusters are surprisingly scarce. The reversible reactions of type 1 are, apart from academic interest, also of practical importance in many homogeneous catalytic processes [2].

$$n\, M_{x/n}(CO)_{(y+z)/n} \rightleftharpoons M_x(CO)_y + z(CO) \qquad (1)$$

One of the most important reactions of this class is the reversible transformation between dicobalt octacarbonyl and tetracobalt dodecacarbonyl (eq. 2):

$$2\, Co_2(CO)_8 \underset{b}{\overset{a}{\rightleftharpoons}} Co_4(CO)_{12} + 4\, CO \qquad (2)$$

---

* Dedicated to Professor Helmut Behrens on the occasion of his 65th birthday on May 30, 1980.

It was known from the very beginnings of metal carbonyl chemistry that dicobalt octacarbonyl, when heated to temperatures between 53—100°C, was quantitatively converted to "cobalt tricarbonyl" [3]. Mond et al. stated, however, that "no re-combination of the products takes place between 15°C and 60°C...". Adkins and Krsek [4], who were the first to realize the homogeneous nature of the "oxo" reaction and the role of cobalt carbonyls therein, seem to have formulated for the first time the reversible character of reaction 2.

Only two papers can be found in the literature, both published more than 20 years ago, which contain quantitative data concerning this equilibrium [5,6]. Ercoli and Barbieri-Hermitte [5] determined the equilibrium constant in the temperature region between 73 and 137°C for the neat melt, i.e. without solvent. Their data were based upon the measurement of carbon monoxide pressure over different amounts of an equilibrated mixture of the two complexes. These authors obtained a mean ΔH^0 value of 33 kcal/mole.

The only study of equilibrium 2 in solution seems to be that of Natta, Ercoli and Castellano [6]. In the course of their study of the oxo-reaction, they obtained approximate values of the equilibrium constant at 110°C and 120°C, in a solvent composed of 33 wt.% cyclohexene and 67 wt.% toluene. These studies were also based on pressure measurements.

We needed the knowledge of the equilibrium composition of the two carbonyls of cobalt in a broad temperature range and in an inert solvent (n-hexane) for two of our current studies: a) high-temperature IR-spectrum of $Co_2(CO)_8$ under CO pressure [7] and b) kinetics of the "backward" reaction (b) of the equilibrium 2 [8], since we were reluctant to apply the values obtained for the melt, or for solvents which we cannot consider inert towards these carbonyls. E.g. complexes of the type (arene)$Co_4(CO)_9$ have been obtained starting from $Co_4(CO)_{12}$, as well as from $Co_2(CO)_8$ in an arene solvent, at temperatures between 50 and 100°C [9]. Since nothing is known about the possible existence of equilibria 3 and 4, one cannot exclude a priori the possibility that the values deduced by Natta et al. [6] were the gross result of a combination of the values of the "basic" equilibrium 2 with 3 and 4.

$$Co_4(CO)_{12} + C_6H_5CH_3 \rightleftharpoons (C_6H_5CH_3)Co_4(CO)_9 + 3\ CO \qquad (3)$$

$$Co_2(CO)_8 + n\text{c.-}C_6H_{10} \rightleftharpoons Co_2(CO)_{8-n}(\text{c.-}C_6H_{10})_n + nCO \qquad (4)$$

The extremely important role of the solvent used is also shown by the fact that a half-life of ~80 days is obtained [8] for reaction 2b at room temperature even under ~8 bar of CO pressure, while this reaction is reported to proceed smoothly with 1 atm of CO only, if isopropanol is used as solvent [1].

We therefore measured the equilibrium concentrations in the system represented by eq. 2 in hexane solution, by a direct quantitative IR spectroscopic method.

We believe that these results are representative for all alkane solvents if differences in the solubility of CO are taken into consideration.

Experimental

Chemicals. Hexane (Fluka A.G. product, pract. grade: >95% normal isomer) was dried over and distilled from $LiAlH_4$. Dicobalt octacarbonyl was prepared by the method of Szabó et al. [10].

Solutions were prepared, by weight, under CO. Carbon monoxide was prepared in the large-scale CO-production equipment of this laboratory, by catalytic dehydration of formic acid. Its v.p.c. purity was better than 99.9%, and its H_2 and O_2 content was of the order of 0.01% (v.p.c.).

The IR-spectroscopic quantitative analysis of the equilibrated solutions was based upon the bridging C—O stretching bands, according to our previously reported method [8].

The reactions were carried out in a thermostated autoclave of 1000 ml total capacity, equipped with a magnetically activated stirrer, gas and liquid inlet valves and sampling tube. Samples were transferred directly into a high pressure infrared cell through a pressure tube. Spectra were scanned under "semi-in-situ" conditions i.e. under working pressure, but at the temperature of the spectrometer (37—38°C), for the following reasons: i) the serious changes in the relative intensities and band forms, mainly of $Co_2(CO)_8$ at higher temperatures, would have rendered a quantitative interpretation of spectra at varying temperatures very difficult; ii) solvent compensation would have been impossible as no heated variable path cell for the reference beam was available.

Upon cooling the solution from the temperature of the experiment (105—145°C) to that of the spectrometer (~38°C), the equilibrium shifts, in principle, in favour of $Co_2(CO)_8$. However, we know from our kinetic measurements [8] that at 37°C, and under the pressures applied in this study (7—14 bar) the half life of reaction 2b lies between 20 and 40 days. Hence the shift of the composition during scanning is negligible.

Spectra were scanned by a Perkin-Elmer Model 325 spectrophotometer. The slit program used was 4.5 corresponding to a spectral slit width of 0.87 cm^{-1} at 1900 cm^{-1}. The scanning speed was 5—8 cm^{-1}/minute. Spectra were recorded linear in absorbance between 1885 and 1810 cm^{-1} with 10 × abscissa expansion (i.e. 1 cm^{-1} = 4 mm). Each spectrum was recorded at least twice.

Solvent absorption was compensated by the use of a variable path cell, and the reduction of the beam cone caused by the pressure cell was compensated by a reference beam attenuator.

The half life of the equilibration in the region of our experiments was in the range between 15 minutes and ca. 2 hours [8]. These values were taken into account while selecting the sampling intervals.

Results

The pressure and temperature region which can be covered conveniently by this kind of measurement is limited by the equilibrium itself, by the rate of the reaction and by the "overall" thermal stability of the cobalt carbonyls towards decomposition according to:

$$Co_x(CO)_y \rightarrow x\,Co + y\,CO \qquad (5)$$

Fortunately, reaction 5 is autocatalytic [11] and very slow in the initial period. In fact, we were able to perform measurements at 145°C under 12 and 14 atm CO pressure, i.e. at conditions which apparently lie outside of the region of stability, for about 2 hours before the diminution of the bands of both carbonyls (maintaining their relative concentrations as determined by equilibrium 2), due to decomposition 5, started. Higher pressures at this (or higher) temperature shift the equilibrium completely towards the $Co_2(CO)_8$ side.

On the low temperature side, e.g. 100°C, CO pressures between 2 and 6 atm are required in order to obtain equilibrium mixtures which can be accurately evaluated by the analytical method applied. Under these conditions, however, half-lives of the reaction around 5 to 10 hours are found, and extremely long times are needed to make sure that equilibrium has been reached. Within these limits 17 points were determined (Table 1). The concentration values were evaluated from IR spectra, and the carbon monoxide partial pressure was calculated from total pressure and solvent vapour pressure as described earlier [8]. The equilibrium constant was defined as follows:

$$K_p = \frac{[Co_4(CO)_{12}]p_{CO}^4}{[Co_2(CO)_8]^2} \tag{6}$$

or with $[CO] = p_{CO}\alpha$

$$K = \frac{[Co_4(CO)_{12}][CO]^4}{[Co_2(CO)_8]^2} = K_p\alpha^4 \tag{7}$$

where $\alpha = 0.012$ mol dm^{-3} bar^{-1} was used as the solubility constant of carbon monoxide in hexane and assumed to be independent of temperature and pressure within the range of conditions of our experiments (cf. [8], footnote on page 308). (Square brackets denote molarities at equilibrium).

The temperature dependence of K_p was determined by a linear least squares

TABLE 1

EXPERIMENTAL VALUES OF THE EQUILIBRIUM CONSTANTS AT DIFFERENT TEMPERATURES AND CARBON MONOXIDE PRESSURES

Temperature (°C)	CO partial pressure (bar) [a]	$K_p \times 10^{-5}$ (bar^4 dm^3 mol^{-1})	$K \times 10^3$ (mol dm^{-3})^3
105	6.0	0.55	1.13
119	6.7	2.87	5.95
119	7.7	2.58	5.34
119	8.7	2.55	5.28
119	9.6	2.44	5.05
119	10.6	2.30	4.77
119	11.3	2.22	4.61
119	11.5	2.29	4.74
113	11.5	2.39	4.95
129	11.5	6.46	13.4
129	11.5	5.97	12.4
129	11.5	6.30	13.1
129	12.4	6.05	12.6
129	13.4	5.91	12.2
129	13.4	6.13	12.7
145	11.4	25.5	52.9
145	13.3	24.4	50.5

[a] 1 bar = 10^5 Pa ≙ 0.98692 atm.

TABLE 2

CALCULATED ENTHALPY AND ENTROPY OF REACTION FOR THE EQUILIBRIUM 2

$\Delta H^0 =$	29.5 ± 0.5 kcal mol^{-1}	$\hat{=} 124 \pm 2$ kJ mol^{-1}
$\Delta S^0 =$	135 ± 3 cal mol^{-1} K^{-1}	$\hat{=} 565 \pm 12$ J mol^{-1} K^{-1}
$\Delta S^0_p =$	100 ± 3 cal mol^{-1} K^{-1}	$\hat{=} 418 \pm 12$ J mol^{-1} K^{-1}

95% confidence interval given. 1 cal $\hat{=}$ 4.186 J.

fit yielding the empirical equation

$$\log K_p = 21.84 - 6455/T \ (K_p \text{ in bar}^4 \text{ dm}^3 \text{ mol}^{-1}) \tag{8}$$

The reaction enthalpy ΔH^0_p and entropy ΔS^0_p (based on the standard state $p_{CO} = 1$ bar and unity activity coefficients) were derived from the regression parameters. Assuming the enthalpy of solution of CO, ΔH^0_s, to be negligible, reaction parameters referring to the standard state [CO] = 1 mol dm^{-3} and to the equilibrium constant K were calculated as follows:

$$\Delta H^0 = \Delta H^0_p - 4\ \Delta H^0_s \sim \Delta H^0_p \tag{9}$$

$$\Delta S^0 = \Delta S^0_p - 4\ R \ln \alpha \tag{10}$$

and are compiled in Table 2. Our value of ΔH^0 = 29.5 kcal mol^{-1} agrees quite well with the range of 29.7 to 34.5 kcal mol^{-1} given by Ercoli et al. [5] for a cobalt carbonyl melt at 73—137°C. For obvious reasons it is not possible to derive a comparable value for the reaction entropy from their data. But from the stoichiometry of the reaction a rather large positive value for ΔS^0 has to be

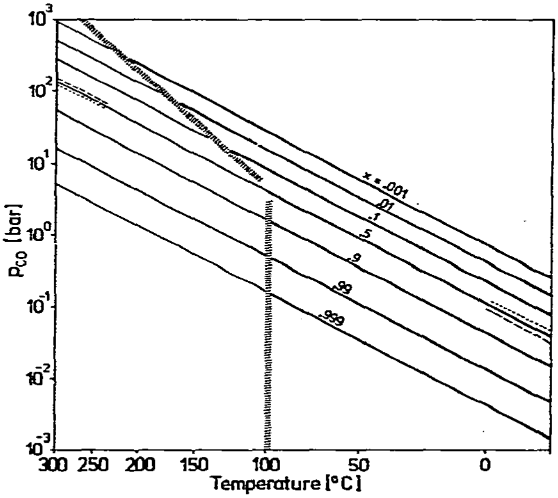

Fig. 1. Equilibrium composition as a function of temperature and carbon monoxide pressure in hexane. (x = fraction of $Co_4(CO)_{12}$ as defined in eq. (11); total cobalt concentration: 0.02 mol dm^{-3}). Uncertainty (based on the corresponding 95% confidence interval for ΔS^0 and ΔH^0) is indicated at low and high temperature for x = 0.5. For details on the shaded zones refer to the text.

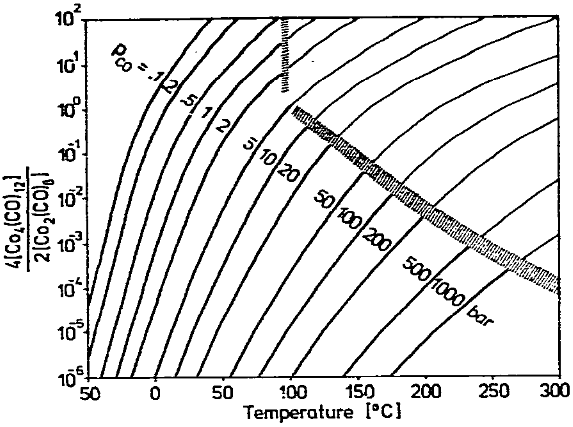

Fig. 2. Molar ratio of cobalt present in the form of $Co_4(CO)_{12}$ and $Co_2(CO)_8$ at equilibrium vs. temperature at constant carbon monoxide partial pressure. (Total cobalt concentration: 0.02 mol dm^{-3}. For details of the shaded zones refer to text.)

expected. It is worth mentioning that a ΔH^0 of 36.3 (± ~10) kcal/mol can be calculated from enthalpies of formation ΔH_f^0 (gaseous phase, 298 K) given by Connor et al. [12].

For better practical applicability our results are shown also in two different graphical representations, both referring to 0.02 mol dm^{-3} total cobalt concentration. Fig. 1 is a log p_{CO} vs. $1/T$ plot, where straight lines represent constant fractions, x, of cobalt in the form of $Co_4(CO)_{12}$ according to eq. 1. Fig. 2 is a log

$$x = \frac{4[Co_4(CO)_{12}]}{4[Co_4(CO)_{12}] + 2[Co_2(CO)_8]} \tag{11}$$

$(4[Co_4(CO)_{12}]/2[Co_2(CO)_8])$ vs. temperature representation in which each curve corresponds to a constant p_{CO} value, as indicated.

Both graphs contain, as a shaded zone, the approximate border of overall thermal stability towards decomposition to metal and carbon monoxide, as calculated from the results of Berty, Oltay and Markó [13]. The vertical limiting zone at 96—100°C is based on the report of Baev [14], and is only tentative (see comments in the Discussion). As reported earlier by Markó [11] and also observed in the present study, the formation of $Co_2(CO)_8$ from metallic cobalt and CO, as well as its decomposition are autocatalytic and in the initial phase quite slow. Hence in the region beyond the (not completely sharp) stability border the two cobalt carbonyls are present in a mestable state and in equilibrium with each other. This is reflected by the finer lines in those parts of the plots.

Discussion of the stability regions of $Co_2(CO)_8$ and $Co_4(CO)_{12}$

Our results permit us, for the first time, to define in quantitative terms the temperature and carbon monoxide pressure conditions which are needed for the thermodynamic stability of the two simple cobalt carbonyls.

As Figs. 1 and 2 show, without carbon monoxide $Co_2(CO)_8$ is thermodynamically unstable, even if kept at subzero temperatures, although its conversion to $Co_4(CO)_{12}$ is then kinetically very slow [15]. However, $Co_2(CO)_8$ is converted quantitatively to $Co_4(CO)_{12}$ even at room temperature if it is kept under vacuum: we find a half-life of ca. 9 hours for this reaction at 20° C, and of ca. $1\frac{1}{4}$ h at 28° C (under a total pressure of 0.02 to 0.05 Torr over a 1.7×10^{-2} and 0.6×10^{-2} molar solution, respectively, of $Co_2(CO)_8$ in hexadecane, stirred with ca. 1000 rpm, in darkness). The previously reported [3] temperature of 53°C needed to accomplish this conversion corresponds to an equilibrium containing ca. 99% $Co_4(CO)_{12}$ at 0.1 bar CO pressure.

$Co_2(CO)_8$ is thermodynamically stable up to 5°C if kept under 1 atm of carbon monoxide (equilibrium concentration of $Co_4(CO)_{12} < 0.1\%$); however, at 25°C ca. 3% of $Co_4(CO)_{12}$ is present at equilibrium under 1 atm of CO. On the other hand $Co_4(CO)_{12}$ is thermodynamically stable only if the CO partial pressure is very low: 0.1 atm or less. Under 1 atm of carbon monoxide, at about 53 (± 2)°C it would convert to a solution where 50% of the cobalt content is present in the form of $Co_2(CO)_8$; however, with a half-life of about 160 days [8]. At room temperature, thermodynamics demand that the partial pressure of CO should not exceed 10 Torr for the stability of $Co_4(CO)_{12}$. It is however kinetically inert up to several atmospheres of CO [8].

Nothing is known in unequivocal quantitative terms, as yet about the high temperature limit of the stability region of $Co_4(CO)_{12}$ and about the thermal formation of a species with a lower CO/Co ratio prior to complete decomposition to metallic cobalt and CO. Orekhova and Baev reported that, in the solid state, thermal decomposition of $Co_4(CO)_{12}$ to metallic cobalt starts only above 100°C [14].

On the thermal formation of $Co_6(CO)_{16}$ contradictory observations are reported. According to Chini $Co_6(CO)_{16}$ decomposes under nitrogen at 110—120° C under vacuum (0.001 Torr) at 70—80°C [16] and it is not formed thermally from $Co_4(CO)_{12}$ [17]. However, $Co_6(CO)_{16}$ should convert to $Co_4(CO)_{12}$, in toluene solution, under 1 atm carbon monoxide, even at room temperature. In contrast, Lewis et al. reported that $Co_4(CO)_{12}$ is converted to $Co_6(CO)_{16}$, under vacuum, without solvent between 63—100°C [18]. We could not observe the formation of $Co_6(CO)_{16}$ from $Co_4(CO)_{12}$ or $Co_2(CO)_8$ (as checked by the absence of the bridging band at 1791 cm^{-1} [19]) when the solution was kept in an autoclave under vacuum (i.e. under only the partial pressure of hexane) for several days at 70—90°C, or 24 hours at 100°C. At and above 100°C we observed the slow thermal decomposition to metallic cobalt and carbon monoxide as mentioned before.

These not entirely consistent observations indicate that the temperature region between 70—120°C, in the presence of very low CO partial pressures, is still to be explored.

Acknowledgments

We thank Professor P. Pino for his support and interest, Mr. J.-J. Parnaud for samples of dicobalt octacarbonyl and Mr. R. Laubbacher for gas chromatographic analyses. This work was supported by the Schweizerischer Nationalfonds zur Förderung der Wissenschaftlichen Forschung (No. 2.902-0.77).

References

1 P. Chini and B.T. Heaton, Topics Curr. Chem., 71 (1977) 1.
2 I. Wender and P. Pino, Organic Syntheses via Metal Carbonyls, Vol. 2, J. Wiley, New York, London, Sydney, Toronto, 1977.
3 L. Mond, H. Hirtz and M.D. Cowap, J. Chem. Soc., 97 (1910) 798; idem, Z. Anorg. Allg. Chem., 68 (1910) 207.
4 H. Adkins and G. Krsek, J. Amer. Chem. Soc., 70 (1948) 383.
5 R. Ercoli and F. Barbieri-Hermitte, Atti Accad. Naz. Lincei Cl. Sci. Fis. Mat. Nat. Rend., 16 (1954) 249.
6 G. Natta, R. Ercoli and S. Castellano, Chim. Ind. (Milan), 37 (1955) 6.
7 G. Bor, U.K. Dietler and K. Noack, J. Chem. Soc. Chem. Commun., (1976) 914.
8 G. Bor, U.K. Dietler, P. Pino and A.J. Poë, J. Organometal. Chem., 154 (1978) 301.
9 I.U. Khand, G.R. Knox, P.L. Pauson and W.E. Watts, J. Chem. Soc. Chem. Commun., (1971) 36; idem, J. Chem. Soc. Dalton, (1973) 975; G. Bor, G. Sbrignadello and F. Marcati, J. Organometal. Chem., 46 (1972) 357; A. Sisak, C. Sisak, F. Ungváry, G. Pályi and L. Markó, ibid., 90 (1975) 77.
10 P. Szabó, L. Markó and G. Bor, Chem. Techn. (Leipzig), 13 (1961) 549.
11 L. Markó, Magy. Kem. Lapja, 13 (1958) 386.
12 J.A. Connor, H.A. Skinner and Y. Virmani, Faraday Symp. Chem. Soc., 8 (1973) 18.
13 J. Berty, E. Oltay and L. Markó, Chem. Techn. (Leipzig), 9 (1957) 283.
14 S.E. Orekhova and A.K. Baev, 5th Internat. Conf. Organometal. Chem., 1971, Moscow, Abstr. No. 356; c.f. Gmelins Handbuch der anorganischen Chemie, Ergänzungswerk zur achten Auflage, Band 6: Kobaltorganische Verbindungen, Vol. II, p. 46, Verlag Chemie, Weinheim/Bergstrasse, 1973.
15 F. Ungváry and L. Markó, J. Organometal. Chem., 71 (1974) 283.
16 P. Chini, Inorg. Chem., 8 (1969) 1206.
17 S. Matinengo, P. Chini, V.G. Albano, F. Cariati and T. Salvatori, J. Organometal. Chem., 59 (1973) 379.
18 C.R. Eady, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Dalton, (1975) 2606.
19 F. Cariati, V. Valenti, and P. Barone, Gazz. Chim. Ital., 99 (1969) 1327.