ELSEVIER

Journal of Organometallic Chemistry 570 (1998) 39–47

Journal of Organo metallic Chemistry

Fundamental metal carbonyl equilibria, V[1]: Reinvestigation of the equilibrium between dicobalt octacarbonyl and cobalt tetracarbonyl hydride under hydrogen pressure

Rina Tannenbaum [2,a,*], Urs K. Dietler [3,b], György Bor [4,b], Ferenc Ungváry [c]

[a] *Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA*
[b] *Department of Industrial and Engineering Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland*
[c] *Department of Organic Chemistry, University of Veszprém, P.O.Box 158, H-8201 Veszprém, Hungary*

Received 15 April 1998; received in revised form 5 June 1998

Abstract

The equilibrium reaction of dicobalt octacarbonyl with dihydrogen is regarded as one of the key steps in the activation of hydrogen by cobalt carbonyls. This has been reconfirmed in recent years by important new observations regarding the versatile chemistry of the cobalt hydride complex. Although the nature of the molecule responsible for the splitting of the transiently formed $RCO{\cdot}Co(CO)_3$ in the hydroformylation reaction is still the subject of discussions, the essential importance of the cobalt tetracarbonyl hydride is evident and undisputed. This paper presents a critical review of the existing data on the equilibrium reaction of dicobalt octacarbonyl with dihydrogen, along with the results of new infrared spectroscopic measurements under semi in-situ conditions. The equilibrium constant, $K_p = [HCo(CO)_4]^2/[Co_2(CO)_8]\cdot pH_2$ ($mol\cdot l^{-1}\cdot bar^{-1}$), obtained from these latter measurements in hexane as solvent, depends on temperature in the 50.7–117.0°C range according to the equation log $K_p = -(0.670 \pm 0.106)–(886 \pm 38)/T$. The van't Hoff plot of these data yielded the thermodynamic parameters $\Delta H = 4.054 \pm 0.175$ $kcal\cdot mol^{-1}$ and $\Delta S = -3.067 \pm 0.488$ $cal\cdot mol^{-1}\cdot K^{-1}$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Dicobalt octacarbonyl; Cobalt hydride complex; Hydroformylation reaction

---

1. Introduction

Roelen [2] and Adkins and Krsek [3] were the first to independently suggest that cobalt tetracarbonyl hydride, $HCo(CO)_4$, is "the reagent effective in the synthesis" of aldehydes from olefins with carbon monoxide and hydrogen under pressure. Several years earlier, Hieber, Schulten and Marin [4] had discovered that the decomposition of $HCo(CO)_4$ to $Co_2(CO)_8$ and dihydrogen is a reversible reaction, and the formation of cobalt tetracarbonyl hydride from dicobalt octacarbonyl can be observed under high pressure as in Eq. (1):

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4. \qquad (1)$$

It has been generally accepted ([5]a, b, [6]) that $HCo(CO)_4$ is only a catalyst precursor in the hydroformylation and related reactions. The true catalytic species, according to the mechanism first suggested by Heck [7], is postulated to be the 16-electron species, $HCo(CO)_3$. Evidence for its existence (at least at low temperatures) has been presented by matrix isolation experiments combined with infrared spectroscopic mea-

---

* Corresponding author.

[1] Reference [29][b] should be considered as Part IV; for Part III see reference [1].

[2] Part of the Ph.D. Dissertation performed in the Department of Industrial and Engineering Chemistry at the Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, 1982.

[3] Present address: Electrowatt Engineering Services Ltd., Zürich, Switzerland.

[4] Retired; Honorary Professor Emeritus in the Department of Organic Chemistry, University of Veszprém, P.O. Box 158, H-8201 Veszprém, Hungary.

PII S0022-328X(98)00798-0

surements by Orchin et al. [8]. The pathway to this complex involved the formation of another electron-deficient species, $Co_2(CO)_7$. However, recent studies by Klinger and Rathke [9] devoted to the estimation of the relative energetics of the Co–Co bond homolysis process and carbonyl exchange, suggest that the formation of such a coordinatively unsaturated species under the conditions used for the hydroformylation reaction is energetically unfavorable.

In any case, equilibrium reaction (Eq. (1)) must be regarded as one of the key steps in hydrogen activation by cobalt carbonyls, as has been reconfirmed in recent years by important new observations regarding the versatile chemistry of $HCo(CO)_4$. Wegmann and Brown [10] and independently Ungváry and Markó [11], reported on the effect of $Co_2(CO)_8$ on the decomposition of $HCo(CO)_4$ to dicobalt octacarbonyl and dihydrogen presenting somewhat different kinetic equation for a radical pathway of this reaction.

Fachinetti has reported ([12]a, b) that in pentane or hexane solutions containing about equimolar quantities of $HCo(CO)_4$ and $Co_2(CO)_8$, the unstable trinuclear hydride, $HCo_3(CO)_9$, characterized recently also by X-ray diffraction analysis ([13]a, b), is formed transiently according to Eq. (2):

$$HCo(CO)_4 + Co_2(CO)_8 \rightarrow HCo_3(CO)_9 + 3CO\uparrow. \qquad (2)$$

To account for the kinetic observations in the stoichiometric hydroformylation of cyclopentene, during which an increase of the concentration of $HCo(CO)_3$ must be accounted for [14], Orchin et al. suggested early on the existence of the irreversible bimolecular reaction shown in Eq. (3):

$$HCo(CO)_4 + Co_2(CO)_7 \rightarrow [HCo_3(CO)_{11}] \rightarrow Co_2(CO)_8 + HCo(CO)_3. \qquad (3)$$

Hence, the possibility of the transient formation of the intermediate $[HCo_3(CO)_{11}]$ gained in probability, since it can be closely related to $HCo_3(CO)_9$ [12], which is prepared by a different method and characterized unequivocally, and also observed directly during the stoichiometric hydroformylation experiments conducted either in the absence of CO, or under very low CO partial pressure ($p_{CO} < 0.6$ atm) [15–17]. Other possible catalytic species have been proposed by Sweany and Russell [18,19] which involve the coordination of a dihydrogen molecule (rather than a CO molecule) to the 16-electron $HCo(CO)_3$ to form $H(H_2)Co(CO)_3$, but spectroscopic evidence of the existence of such a trihydride species is not straightforward.

Although the crucial problem of the hydrogen activation in the hydroformylation reaction, i.e. if the transiently formed $RCO \cdot Co(CO)_3$ is split by dihydrogen, or by $HCo(CO)_4$, is still the subject of discussions ([20]a, b, [21–23], the essential importance of the cobalt tetracarbonyl hydride in these reactions is evident and undisputed.

In the light of this renewed interest in the chemistry of $HCo(CO)_4$, it is surprising how conflicting are the various data on its formation through the reversible reaction (Eq. (1)). This equilibrium was investigated systematically for the first time by Ungváry (in n-heptane solution, and at 35–155°C temperature range). Acidimetric titration of $HCo(CO)_4$ on withdrawn samples followed by a sophisticated calculational procedure was used to obtain the relevant concentration data [24]. The values for the equilibrium constant were completely consistent in of themselves, though there was not the same extent of agreement with earlier data of lesser thoroughness, obtained in toluene as a solvent by other authors [25,26].

In 1976, Alemdaroglu reported new, but substantially different equilibrium values measured by in-situ high pressure IR spectroscopy [20]. This author obviously hoped that his more direct analytical approach would prove superior to the indirect one.

Some time later, Slocum summarized [27] in a graph some new (unpublished) results of Feder and Rathke [28], together with some of Ungváry's earlier values. There seemed to be a fair agreement, though a critical evaluation and comparison was not possible since neither the original values of Rathke and Feder nor any additional information apart from the equilibrium constants (expressed as K_p values) were available.

Some time later, Mirbach [21] published a very thorough kinetic study of reaction (1), and expressed doubts on the reliability of the results of Alemdaroglu on the same topic [20].

In view of the continuing controversy, and since we also felt considerable doubt about the feasibility in this case of a "true in-situ" IR spectroscopic method (see Section 4) as claimed by Alemdaroglu, we decided to reexamine this equilibrium reaction by our own proven semi-in-situ, high pressure/high temperature IR spectroscopic method. The experimental technique adopted will be described in detail in order to familiarize the reader with its pitfalls and the basic facts for a critical comparison of the different results.

We would like to comment also on the delayed publication. The experimental work was performed in the course of the Ph.D. work of one of the authors (R.T., ref. [15]) in the period 1978–1982. Subsequently, during the course of the evaluation of the data and the comparison with other reversible carbonyl systems, the necessity of the reassessment of the solubility data of hydrogen and carbon monoxide in alkane solvents under high pressure and at various temperatures was recognized. This data was then acquired as part of the experimental work in two more recent theses, related to the study of the reversible reactions of ruthenium carbonyls ([29]a, b), and of mixed cobalt/rhodium car-

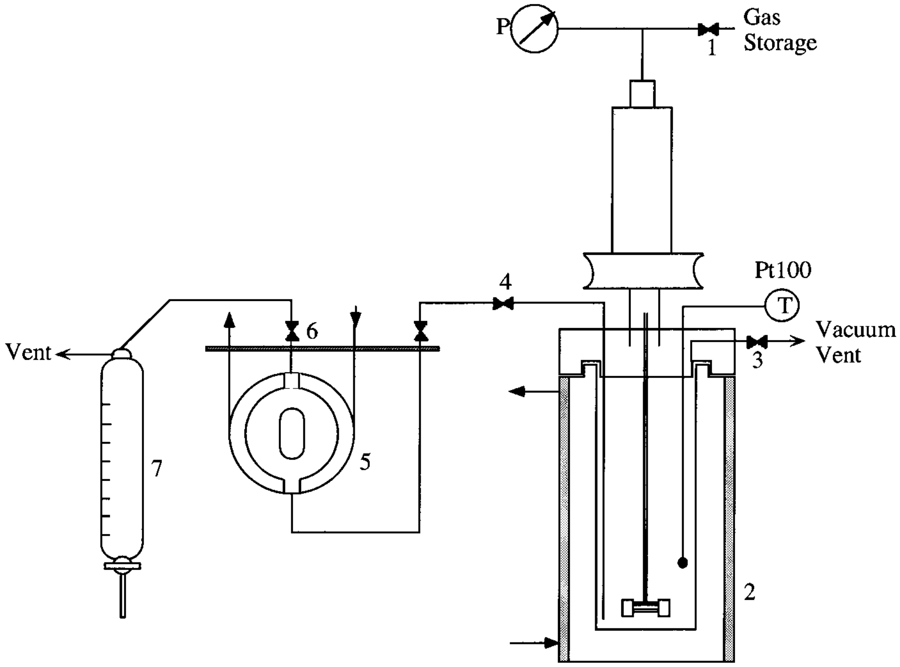

Fig. 1. Reaction apparatus consisting of a stainless steel autoclave of 1093 cm^3 total capacity, equipped with a magnetically operated packless stirrer. Special features: gas inlet (1), autoclave (2), vent valve (3), sampling tube (4), high pressure/high temperature infrared liquid cell (5), IR cell sampling tube (6), sample collection (7).

bonyls ([30]a, b) respectively. The delay in publication of the recent results is owing mainly to these additional studies. The possibility of evaluating the experimental material jointly with the author who made the first measurements of this system (F.U.) gave an additional impulse to the present publication.

Some aspects of these results were initially shown in the Ph.D. thesis of R. Tannenbaum [15] and later published in a paper dealing with the general aspects of the thermodynamics of metal carbonyl clusters [31]; details concerning the infrared spectroscopic studies on dicobalt octacarbonyl with deuterium or hydrogen-deuterium mixtures, respectively, were also published in recent years [32].

2. Experimental

2.1. Chemicals

Hexane (Fluka AG, Buchs, “Practical” grade: > 95% normal isomer) was refluxed over and distilled from $LiAlH_4$ under carbon monoxide or nitrogen. Dicobalt octacarbonyl was prepared by the method of Szabó et al. [33]. Solutions of known concentration (between 5 and 7 mmol l^{-1}) were prepared, by weight, under carbon monoxide.

Hydrogen (“Repurified”, product of the Sauerstoff- and Wasserstoff-werke, Luzern, 99.999% pure) was mixed with known amount (1–35% vol.) of carbon monoxide (prepared by catalytic dehydration of formic acid, washed with potassium hydroxide, compressed and dried by molecular sieve) in order to suppress decomposition of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ [34]; the compressed gas mixtures were stored in aluminum pressure cylinders to avoid formation of iron carbonyls.

2.2. Equipment and procedure

The equilibration reactions were carried out in the following apparatus, as shown in Fig. 1. A stainless steel autoclave of 1093 cm^3 total capacity, equipped with a magnetically operated, packless stirrer (“Dispersimax”: Autoclave International, Erie PA 16512), gas (1), liquid inlet (2), vent valves (3), sampling tube (4), a calibrated manometer with $\pm 1\%$ accuracy, and a platinum resistor thermometer (Pt 100), served as reaction vessel. The autoclave was heated by circulating oil from a thermostated oil bath through the heating jacket. The temperature of the reaction solution was be kept constant to within ± 0.2°C.

For a set of experiments ca. 650 cm^3 of solution were transferred by suction into the well purged autoclave under anaerobic conditions, pressurized immediately with the appropriate gas mixture to approximately 80% of the envisaged pressure, and heated to equilibrium temperature. Then the total pressure was adjusted to the desired value. In regular intervals, fresh samples of the reaction mixture were brought under pressure into a flow-through type high-pressure infrared cell (5)

[15,35,36] connected to the sampling tube (4) by opening the discharge valve (6) leading to a separator, while the pressure in the whole assembly was maintained constant by simultaneously admitting CO/H_2 mixture from the gas storage through the appropriate valve (1). Although the cell is thermostated to any desired temperature, it was kept at instrument temperature (37–38°C) rather than at reaction temperature, in order to avoid difficulties due to changes of the spectrum with temperature, caused by the change of isomeric equilibrium of different forms of $Co_2(CO)_8$ (c.f. [37] and Section 4). Repeated registration of the spectrum proved that the composition of the sample in the cell under these "semi-in-situ" conditions did not change noticeably during scanning. Solvent absorption was compensated for by the use of a commercial variable path length cell. This variable solvent cell also served as indicator for the optical path in the main cell, which varied between 0.028 and 0.033 cm^{-1}. Spectra were scanned by a Perkin-Elmer model 325 grating infrared spectrophotometer. Scanning conditions were: slit program 4.5, spectral slit width 0.87 cm^{-1} (at 1900 cm^{-1}), scanning rate 5–8 cm^{-1} min^{-1}, scanning range 2150–1800 cm^{-1}. Since the temperature of the IR cell was kept at 38°C, the reaction in the cell proceeded at a lower rate than in the autoclave, and hence we were not particularly concerned with the length of time necessary to complete a spectrum ($\sim$ 1 h). Moreover, since these were equilibrium studies, only the last of three consecutive unchanged spectra was used in calculations.

3. Quantitative analysis and computational procedure

Molar concentrations of $HCo(CO)_4$ (I), $Co_2(CO)_8$ (II) and (as far as necessary) $Co_4(CO)_{12}$ (III) in solution in the cell (at 38°C), $[X]_{38,P}$, were calculated from measured intensities of the analytical bands at 2116.0 cm^{-1} (1), 1857.7 cm^{-1}; (2) and 1867.0 cm^{-1}; (3) as described separately [38]. A typical spectrum of an equilibrated solution of $HCo(CO)_4$ and $Co_2(CO)_8$ at 54.5°C is shown in Fig. 2. The actual concentration values in the reaction mixture, $[X]_{T,P}$, were found by multiplying $[X]_{38,P}$ with the solvent density ratio $\rho_{T,P}/\rho_{38,P}$ [39]. The solvent vapor pressure was calculated according to the following equation:

$$p_{\text{hexane}} = p_{0,\text{hexane}} \cdot \exp\left\{\frac{V}{R \cdot T}\ (P_{\text{tot}} - p_{0,\text{hexane}})\right\}. \qquad (4)$$

The vapor pressure of the pure solvent, p_0, and its molar volume V, both at the temperature of the experiment, were taken from ref. [40]. The vapor pressure contribution of the carbonyls, at the experimental concentration levels, was assumed to be negligible.

Data on the solubility of gases in a variety of organic solvents, especially over a wide range of temperatures and pressures, are still quite rare in the literature. The solubility of H_2 has been measured in n-heptane (-30 to $+50$°C, 1 bar) and in n-octane (-25 to $+35$°C, 1 bar) by Cook, Hanson and Alder [40], in n-hexane (-60 to $+25$°C, 1 bar) by Katayama and Nitta [41], and in n-heptane (-35 to $+65$°C, 1 bar) by Lachowicz, Newitt and Weale [42]. There is not only a very good agreement between the solubility values in n-heptane by different authors, but the solubility expressed in molar fractions, $x_{(H_2)} = n_{(H_2)}/n_{(H_2)} + n_{\text{solvent}}$, appears to be virtually independent of the molecular weight of the solvent. This same fact has been observed (although not to the same extent) for other poorly soluble gases, e.g. carbon monoxide in a series of homologous solvents, mainly paraffins (c.f. [43], footnote on p. 308).

More recent measurements by Brunner [44] include solubility data of hydrogen in 10 organic solvents, among them in n-hexane at 25, 50 and 100°C, also at high pressures up to 10 MPa (100 bar).

Independent measurements of the solubility of hydrogen in n-hexane were carried out by Koelliker ([29]a), in the temperature range between 20 and 200°C, up to partial pressures of 200 bar, as a part of systematic studies on the three component system n-hexane/CO/H_2. Through the Henry constant reduced for 1 bar

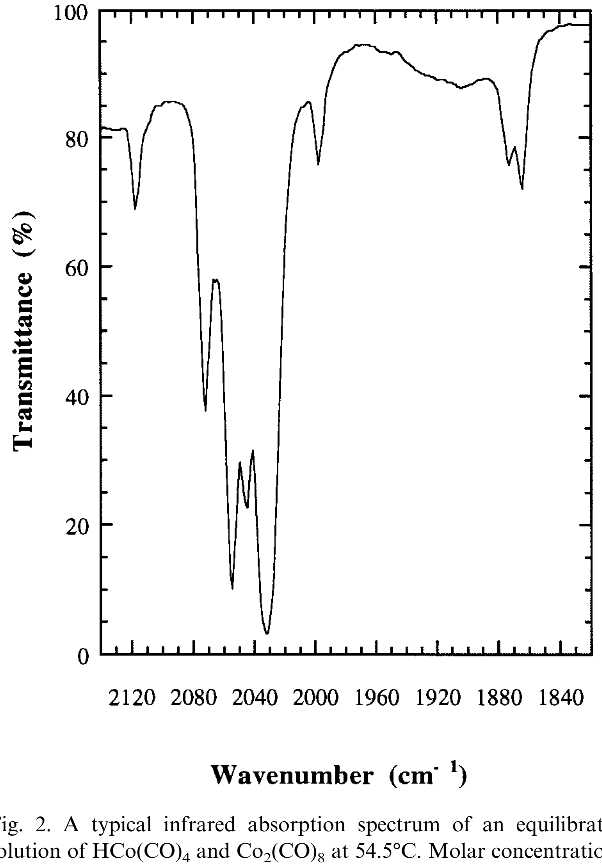

Fig. 2. A typical infrared absorption spectrum of an equilibrated solution of $HCo(CO)_4$ and $Co_2(CO)_8$ at 54.5°C. Molar concentrations of $HCo(CO)_4$ (I), $Co_2(CO)_8$ (II) and $Co_4(CO)_{12}$ (III) in solution were calculated from measured intensities of the analytical bands at 2116.0 cm^{-1} (I), 1857.7 cm^{-1} (II) and 1867.0 cm^{-1} (III).

Table 1
Equilibrium data for the hydrogenation of dicobalt octacarbonyl in n-hexane

Temperature (°C)	p_{tot} (bar)	p_{CO} (bar)	p_{H_2} (bar)	K_c	α	K_p (M atm^{-1})	$1/T$ (K^{-1})	log K_p
50.7	98.7	4.7	93.1	0.064	0.0059	0.00038	0.00309	−3.421
54.9	97.7	4.6	92.1	0.074	0.0060	0.00044	0.00305	−3.356
93.0	98.7	30.0	98.7	0.116	0.0070	0.00081	0.00273	−3.090
98.5	90.7	27.6	90.7	0.117	0.0071	0.00083	0.00269	−3.081
101.5	98.8	30.1	98.8	0.136	0.0072	0.00098	0.00267	−3.010
108.5	98.1	29.9	98.1	0.136	0.0073	0.00100	0.00262	−3.002
117.0	102.0	31.1	102.0	0.154	0.0075	0.00116	0.00256	−2.937

This work: Tannenbaum, Bor and Dietler.

partial pressure, Koelliker obtained by for the solubility of hydrogen, expressed in molar fractions:

$$-\ln X_{(H_2)} = 1.869\cdot 10^{-2}\cdot T - 1.177\cdot 10^{-2}\cdot T^2 + \frac{1.079\cdot 10^3}{T}. \quad (5)$$

The standard deviation of this equation is ± $3.29\cdot 10^{-2}$, which is equivalent to = 0.6 relative%. The measured concentrations found by Koelliker agree excellently (= 0.6%) with those of Brunner [44], and are by about 2.6% higher as compared to those of Katayama [41].

The molar concentration of dissolved hydrogen was calculated according to the following equation:

$$[H_2]_{P,T} = \frac{P_{H_2}(p,T)}{1\ \text{atm}}\cdot\frac{X_{(H_2)}}{1-X_{(H_2)}}\cdot\frac{\rho_{\text{hexane}}{}^{(p,T)}}{MW_{\text{hexane}}}. \quad (6)$$

In Eq. (6), the hydrogen partial pressure was corrected by the standard state conditions ($f^\circ = P^\circ =$ 1 atm). $X_{(H_2)}$ was assumed to be independent of p_{H_2} and p_{tot}.

The equilibrium constant K_c was defined according to:

$$K_c = \frac{[HCo(CO)_4]^2}{[Co_2(CO)_8]\cdot[H_2]}. \quad (7)$$

Slocum's constant [27] is obviously K_p, which is given by:

$$K_p = \frac{[HCo(CO)_4]^2}{[Co_2(CO)_8]\cdot p_{H_2}}. \quad (8)$$

The relationship between the two types of equilibrium constants is given by:

$$\frac{K_p}{K_c} = \alpha \quad \text{where,} \quad \alpha = \frac{[H_2]}{p_{H_2}}. \quad (9)$$

4. Results and discussion

The main objective for this comprehensive summary, was to furnish good data for the scientists and engineers who work with cobalt carbonyl systems under carbon monoxide and hydrogen pressure, in order to enable them to predict the equilibrium concentrations of the different cobalt species at various temperatures and pressures. According to our experience, equations of the type shown in Eq. (10) and diagrams based on these, are very advantageous owing to their simple applicability:

$$\log K_p = A - \frac{B}{T}. \quad (10)$$

Experimental values for the equilibrium constant of reaction (1) were determined at seven different temperatures and hydrogen pressures, and are summarized in Table 1. Carbon monoxide does not take part in the equilibrium reaction, but a certain p_{CO} is necessary to stabilize the participating carbonyl complexes. The equilibrium concentrations were calculated from the experimental in-situ infrared absorbance values, and the K_p values were obtained according to Eq. (9). At this point of the evaluation the only correction applied was the vapor pressure of the solvent hexane. A least-squares treatment of the values shown in Table 1, and plotted in Fig. 3, resulted in the following equation:

$$\log K_p = -0.670 - \frac{886}{T} \quad (11)$$

where, $A = -0.670 \pm 0.106$ and $B = 886 \pm 38$.

Based on this equation, very illustrative graphical representations of this reversible reaction can be obtained; these are similar to the complex-formation (or "titration") curves well known for aqueous complex systems. These graphical representations usually show the ligand concentration as a function of dihydrogen concentration in solution. In the case of a gaseous ligand, this can be substituted by the partial pressure values of the gaseous ligand, as long as the concentration vs. pressure relationship is linear, i.e. the Henry constant does not vary noticeably in the region of the measurement. Fig. 4 shows the isotherm curves obtained for the relative concentrations of $HCo(CO)_4$ as a function of hydrogen partial pressure for a 10^{-3} M l^{-1} initial concentration of $Co_2(CO)_8$.

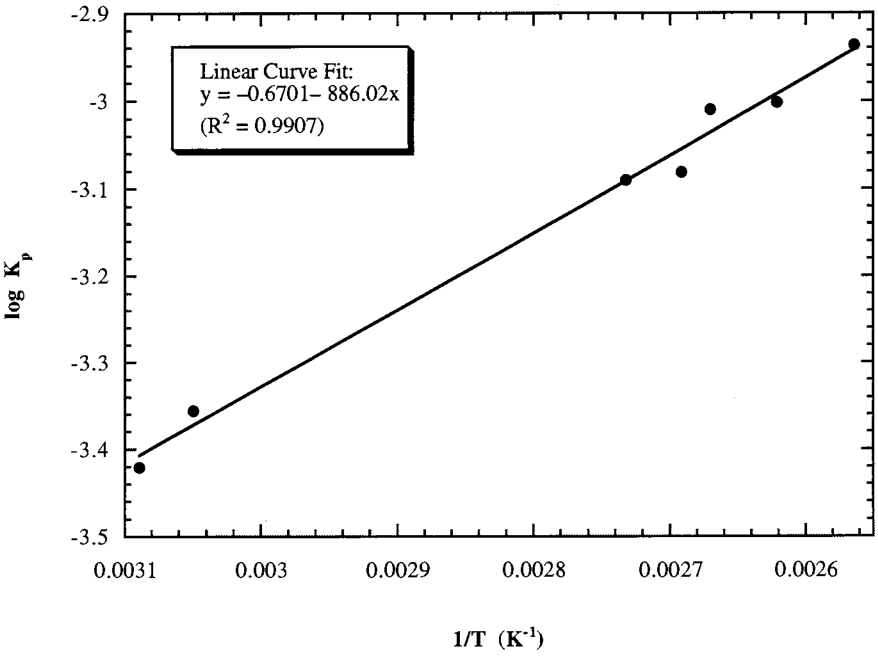

Fig. 3. The van't Hoff plot of our data of K_p as a function of temperature. The equilibrium concentrations were calculated from the experimental in-situ infrared absorbance values, and the K_p values were obtained according to Eq. (9). At this point of the evaluation the only correction applied was the vapor pressure of the solvent hexane.

It is interesting to observe that the curves are very flat and the existence region of $HCo(CO)_4$ spans over more than five orders of magnitude of hydrogen pressure. This is in contrast to the steeper curves obtained for different metal carbonyl equilibrium reactions with carbon monoxide as the entering/leaving ligand[5]. This difference reflects the various stoichiometric coefficients of this ligand in these reactions which enter in the form of powers into the equilibrium equation: the higher the power of the gaseous ligand, the steeper are the curves in this type of representation.

The comparison of these data with the previously published values show that they are very well in line with Ungváry's values, as shown in Fig. 5. Feder and Rathke's results [28] could not be included, since we did not have their original data and hence could not evaluate the method of calculation. However, Slocum [27] had already indicated a very good agreement with Ungváry's results in his ln K_p vs. $1/T$ plot. More recent results obtained by Rathke et al. [45] with respect to the thermodynamics of the hydrogenation of dicobalt octacarbonyl in supercritical CO_2, indicate a very good agreement with both our and Ungváry's data, and are collectively shown in Fig. 5.

The equilibrium data of Alemdaroglu [20] are in disagreement with all the above data, as shown in Fig. 5 as well. This author suggested, by commenting on Ungváry's earlier data, that on taking samples, part of the hydrocarbonyl previously in equilibrium was reconverted to $Co_2(CO)_8$ giving rise to low values for the equilibrium constant. We disagree with this argument in view of rather slow reaction rates and due to the fact that three completely different analytical methods, and different quenching conditions, yielded essentially the same results. Indeed, there are a number of reasons why the results of Alemdaroglu are questionable:

As Slocum pointed out, referring to a personal communication of Penninger (J.M.L. Penninger, personal communication to D. W. Slocum, cf. Ref [27]), Alemdaroglu failed to account for $HCo(CO)_4$ in the vapor phase, and assumed the amount of carbonyl hydride in equilibrium to be equal to the amount of initial $Co_2(CO)_8$ minus unreacted octacarbonyl (measured directly). In contrast, Ungváry calculated (F. Ungváry, personal communication to G. Bor and R. Tannenbaum (1979)) that even at only 64°C, approximately 10% of the hydrocarbonyl was in the vapor phase, giving rise to a true equilibrium constant which is ca. 20% smaller than the one calculated by Alemdaroglu. Since we determined both $Co_2(CO)_8$ and $HCo(CO)_4$ independently and quasi in-situ, this uncertainty was avoided.

Another set of drawbacks is connected to the application of true in-situ IR-spectroscopy (at reaction pressure and reaction temperature) as adopted by Alemdaroglu and his colleagues. It is known that with temperature changes the band shape and position of the

---

[5] The comparison is shown in Figs. 2–5 on p. 546 of [31]; more recent results with molar fraction values rather than pressure of the gaseous ligand are shown on Fig. 7 of [30][b], and Figs. 4 and 5 of [29][b].

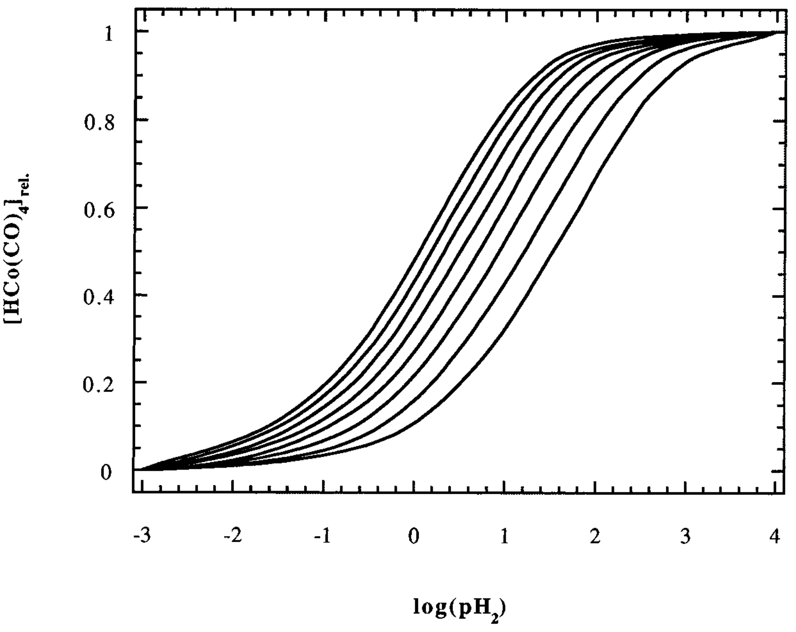

Fig. 4. The isotherm curves obtained for the relative concentrations of $HCo(CO)_4$ as a function of hydrogen partial pressure for a 10^{-3} M l^{-1} initial concentration of $Co_2(CO)_8$.

sharp metal carbonyl bands change considerably making calibration difficult. In the case of $Co_2(CO)_8$, an additional complication arises from the presence of three different isomers [37,46] which coexist in solution and whose equilibrium composition (and hence the spectrum) changes rapidly with temperature. What Alemdaroglu called "the characteristic absorption band of $Co_2(CO)_8$ at 2068 cm^{-1}"is precisely a superposition of two bands (at 2069 and 2071 cm^{-1}) belonging to two different isomers ([37,47]a, b). In view of this and the quality of the published infrared spectrum an error of ~4% postulated by this author for the determination of $Co_2(CO)_8$ is highly optimistic, to say the least.

Based on these considerations we are convinced to have obtained the correct equilibrium concentrations which are well reflected, for practical use, by the equilibrium isotherms in Fig. 4.

Although in some of our earlier studies usually K_c values served for obtaining the corresponding thermodynamic parameters [1,31,34,48], scientifically more exact thermodynamic parameters should be derived from K values which are dimensionless ([29]a, b, [30]a, b). For liquid phase reactions [49], the dimensionless equilibrium constant, K_a, is given by:

$$K_a = \prod_i a_i^{v_i} = \prod_i (x_i \cdot \gamma_i)^{v_i} = \prod_i \left(\frac{C_i}{C} \cdot \gamma_i\right)^{v_i} = C^{\Sigma v_i} K_c \cdot K_\gamma \tag{12}$$

where, a_i, activities of the species, $C_i/C = x_i$, and γ_i, activity coefficients of the species.

Since the reactions are conducted in hydrocarbon solvents (e.g. hexane, heptane), the solutions are non-ionic, and hence γ_i for all species may be approximated to be unity. Therefore, the ratio between K_a and K_c is equal to $C^{-\Sigma v_i}$. Fortunately, in the present case, $\Sigma v_i = 0$ and hence $K_c = K_a$, and is dimensionless as well.

The van't Hoff plot of our data of K_p as a function of temperature shown in Fig. 3, yielded the desired thermodynamic parameters, i.e. changes in the enthalpy and entropy of the reaction, shown in Table 2. Since the activities of gases are more closely related to their pressures rather than their concentrations, the most meaningful comparison is that for which the thermochemical data were derived using K_p values rather than K_c values. A statistical analysis of the data shows that the enthalpy values obtained for the hydrogenation of $Co_2(CO)_8$ in several different media correlate very closely (within a 4% error), while the entropy values correlate more divergently (within a 25% error).

Acknowledgements

The authors thank Dr Jerry Rathke of the Argonne National Laboratory, for very helpful discussions. The authors also thank the reviewers of this manuscript for their constructive criticism. The financial assistance (to R.T.) of the Office of International Education of the University of Minnesota is also appreciated.

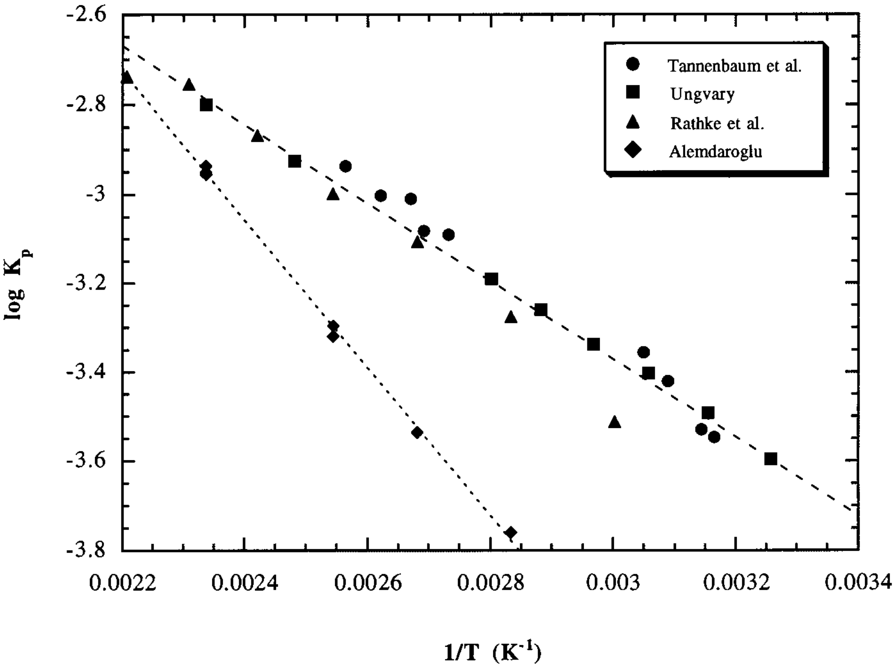

Fig. 5. The van't Hoff plot of all data of K_p as a function of temperature. The comparison of the data shows that those of Alemdaroglu are in disagreement with all other data.

Table 2
Thermochemical parameters for the hydrogenation of dicobalt octacarbonyl

Reaction medium	ΔH (kcal mol^{-1})	ΔH (kcal mol^{-1})
n-hexane^a	4.1	−3.1
n-heptane^b	4.3	−2.6
CO$_2^c$	4.0	−4.2

^{a} This work. $\Delta H = 4.054 \pm 0.175$ (kcal·mol^{-1}) and $\Delta S = -3.067 \pm 0.488$ (cal·mol^{-1}·K^{-1})

^{b} Ungváry, 1972 [24].

^{c} Rathke et al., 1992 [45].

References

[1] F. Oldani, G. Bor, J. Organometal. Chem. 279 (1985) 459.
[2] O. Roelen, Angew. Chem. A 60 (1948) 62.
[3] H. Adkins, G. Krsek, J. Am. Chem. Soc. 70 (1948) 383.
[4] W. Hieber, H. Schulten, R. Marin, Z. Anorg. Allg. Chem. 240 (1939) 261.
[5] (a) P. Pino, F. Piacenti, M. Bianchi, in: I. Wender, P. Pino (Eds.), Organic syntheses via metal carbonyls, Vol. 2. Wiley, New York, 1977. (b) J. Falbe, New syntheses with carbon monoxide, Springer Verlag, New York, 1980.
[6] For a comprehensive review on HCo(CO)$_4$ as a catalyst see: M. Orchin, Acc. Chem. Res., 14, (1981) 251.
[7] R.F. Heck, D.S. Breslow, J. Am. Chem. Soc. 83 (1961) 4023.
[8] P. Werner, B.S. Ault, M. Orchin, J. Organometal. Chem. 162 (1978) 189.
[9] R.J. Klinger, J.W. Rathke, J. Am. Chem. Soc. 116 (1994) 4772.
[10] R.W. Wegman, T.L. Brown, J. Am. Chem. Soc. 102 (1980) 2494.
[11] F. Ungváry, L. Markó, J. Organometal. Chem. 193 (1980) 383.
[12] (a) G. Fachinetti, L. Balocchi, F. Secco, M. Venturini, Angew. Chem., 93 (1981) 215. (b) Angew. Chem. Internat. Ed. Engl., 20 (1981) 204, and pertinent references therein.
[13] (a) G. Fachinetti, S. Pucci, P.F. Zanazzi, U. Methong, Angew. Chem., 91 (1979) 657. (b) Angew. Chem. Int. Ed. Engl. 18 (1979) 619 (b) G. Fachinetti, J. Chem. Soc., Chem. Comm., 397 (1979).
[14] A.C. Clark, J.F. Terepane, Jr., M. Orchin, J. Org. Chem. 39 (1974) 2405.
[15] R. Tannenbaum, Ph. D. Thesis, Swiss Federal Institute of Technology, Dissertation ETH No. 6970, Zürich, Switzerland, 1982.
[16] R. Tannenbaum, G. Bor, 1998, manuscript in preparation.
[17] P. Pino, A. Major, F. Spindler, R. Tannenbaum, G. Bor, I.T. Horváth, J. Organometal. Chem. 417 (1991) 65.
[18] R.L. Sweany, J. Am. Chem. Soc. 104 (1982) 3739.
[19] R.L. Sweany, F.N. Russell, Organometallics 7 (1988) 719.
[20] (a) N.H. Alemdaroglu, Ph.D. Thesis, Technische Hogschool Twente, Twente, The Netherlands, 1974. (b) N.H. Alemdaroglu, J.M.L. Penninger, E. Oltay, Monatshefte für Chemie, 107 (1976) 1043.
[21] M.F. Mirbach, J. Organometal. Chem. 265 (1984) 205.
[22] I. Kovács, F. Ungváry, L. Markó, Organometallics 5 (1986) 209.
[23] M.S. Borovikov, I. Kovács, F. Ungváry, A. Sisak, L. Markó, J. Mol. Catal. 75 (1992) 27.
[24] F. Ungváry, J. Organometal. Chem. 36 (1972) 363.
[25] R. Iwanaga, Bull. Chem. Soc. Japan 35 (1962) 774.
[26] V. Yu. Gankin, D.P. Krinkin, D.M. Rudkovskii, in: D.M. Rudkovskii (ed.), Carbonylation of usaturated hydrocarbons, Khimia, Leningrad, 1968, p. 45.
[27] D.W. Slocum, Catal. Org. Synth. 7 (1980) 245.
[28] H.M. Feder, J.W. Rathke, unpublished results; ref. 38 in [27].
[29] (a) R. Koelliker, Ph. D. Thesis, Swiss Federal Institute of Technology, Dissertation ETH No. 8704, Zürich, Switzerland, 1988. (b) R. Koelliker, G. Bor, J. Organometal. Chem., 417 (1991) 439.
[30] (a) M. Garland, Ph. D. Thesis, Swiss Federal Institute of Technology, Dissertation ETH No. 8585, Zürich, Switzerland, 1988. (b) M. Garland, I.T. Horváth, G. Bor, P. Pino, Organometallics, 10 (1991) 559.
[31] G. Bor, Pure Appl. Chem. 58 (1986) 543.
[32] R. Tannenbaum, G. Bor, Inorg. Chim. Acta 201 (1992) 87.

[33] P. Szabó, L. Markó, G. Bor, Chem. Techn. (Berlin) 13 (1961) 549.

[34] G. Bor, U.K. Dietler, J. Organometal. Chem. 191 (1980) 295.

[35] K. Noack, Spectrochim. Acta 24 (1968) 1917.

[36] U.K. Dietler, Ph. D. Thesis, Swiss Federal Institute of Technology, Dissertation ETH No. 5428, Zürich, Switzerland, 1974.

[37] G. Bor, U.K. Dietler, K. Noack, J. Chem. Soc. Chem. Comm. 914 (1976).

[38] R. Tannenbaum, U.K. Dietler, G. Bor, Inorg. Chim. Acta 154 (1988) 109.

[39] R.W. Gallant, Physical properties of hydrocarbons, vol. 1, Gulf Publ. Company, Houston, 1968, p. 139.

[40] M.W. Cook, D.N. Hanson, B.J. Adler, J. Chem. Phys. 26 (1957) 748.

[41] T. Katayama, T. Nitta, J. Chem. Eng. Data 21 (1976) 194.

[42] S.K. Lachowicz, D.M. Newitt, K.E. Weale, Trans. Faraday Soc. 51 (1955) 1198.

[43] G. Bor, U.K. Dietler, P. Pino, A. Poë, J. Organometal. Chem. 154 (1978) 301.

[44] E. Brunner, J. Chem. Eng. Data 30 (1985) 269.

[45] J.W. Rathke, R.J. Klinger, T.R. Krause, Organometallics 11 (1992) 585.

[46] R.L. Sweany, T.L. Brown, Inorg. Chem. 16 (1977) 415.

[47] (a) K. Noack, Spectrochim. Acta, 19 (1963) 1925. (b) G. Bor, Spectrochim. Acta, 19 (1963) 2065.

[48] F. Oldani, G. Bor, J. Organometal. Chem. 246 (1983) 309.

[49] S.I. Sandler, Chemical and Engineering Thermodynamics, 2nd ed. Wiley, New York, 1989, p. 494–523, and p. 538–545.