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Quantitative IR Spectroscopic Determination of the Concentrations of Cobalt Carbonyl Complexes in a Three-component System*

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Abstract

The three-component system consisting of $Co_4(CO)_{12}$, $Co_2(CO)_8$ and $HCo(CO)_4$ was analyzed by means of IR spectroscopy. A quantitative method was developed in order to enable the precise calculation of the concentrations of all three compounds simultaneously. The quantitative analysis was based upon the intensity of the bridging CO stretching bands at 1858 cm^{-1} (A_2) and 1867 cm^{-1} (A_1) of the polynuclear carbonyls, and the terminal CO symmetric stretching band of $HCo(CO)_4$ at 2116 cm^{-1} (A_3). The mathematical expression for the concentrations of the three compounds required the precise knowledge of at least one of the four extinction coefficients of either $Co_4(CO)_{12}$, ϵ_{J1} and ϵ_{J2}, or $Co_2(CO)_8$, ϵ_{K1} and ϵ_{K2}. The reference extinction coefficient was ϵ_{K2}, because $Co_2(CO)_8$ was employed as the starting compound in all experiments performed in this study. In order to determine the extinction coefficient of $HCo(CO)_4$ at 2116 cm^{-1}, ϵ_3, intensities of this band were plotted as function of the corresponding concentrations of $HCo(CO)_4$, which were calculated by means of the three-component system method; from the slope of the straight line ϵ_3 could be directly calculated.

Introduction

The monitoring of reactions by means of IR spectroscopy represents an unrivaled tool when reaction intermediates are sought, or when reaction kinetics and/or equilibria are studied. However, the quantitative analytical application of IR spectroscopy is handicapped by the severe lack of accurate extinction coefficients for analytically relevant bands of even the most important simple metal carbonyls. The classical papers of Noack [1] and Beck and Nitzschmann [2] on metal carbonyl band intensities did not have analytical aims, and the data of these authors were obtained with instruments which are now technically obsolete.

In the studies on kinetics [3] and equilibria [4, 5] of some catalytically important reactions of cobalt carbonyls with carbon monoxide, hydrogen and olefins, it became necessary to calculate the accurate relative and absolute extinction coefficients of analytically useful absorption bands of $Co_2(CO)_8$, $Co_4(CO)_{12}$ and $HCo(CO)_4$. In an earlier phase of these studies, where only carbon monoxide was involved as the gaseous reactant, an equation had been developed [3] which provided the ability to obtain the relative concentrations of dicobalt octacarbonyl and tetracobalt dodecacarbonyl based on the measurement of the relative intensities of the components of the doublet 1858/1867 cm^{-1}. That equation was based upon numerous observations in a closed system concerning the following reaction

$$Co_4(CO)_{12} + 4CO \rightleftharpoons 2Co_2(CO)_8$$

This reaction was monitored in both directions by IR spectroscopy within temperature and pressure ranges where only these two cobalt carbonyls existed at the same time, and both were thermodynamically stable. This method permitted an accurate determination of the relative values of the intensities at the two analytical frequencies in systems where the cobalt concentration was constant.

For the cobalt carbonyl hydride, $HCo(CO)_4$, no useful intensity data were known. In a study dealing with the force constant calculation of trigonal bipyramidal $LM(CO)_4$ compounds, band intensity ratios were used for the calculation of the CO_{ax}–Co–CO_{eq} angle [6] (result confirmed later by electron diffraction [7]). However, the determination of the extinction coefficients was unsuccessful because of the fast decomposition of the hydride under atmospheric conditions.

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The only attempt known to date [8] to develop and apply a quantitative infrared spectroscopic analytical method for the determination of $HCo(CO)_4$ involved its strongest band at 2030 cm^{-1} as the analytical band. Unfortunately, practically at the same frequency also $Co_2(CO)_8$ has an absorption band, and hence the additivity of the absorbances and the cobalt material balance had to be used in order to obtain indirectly the absorptivities of $HCo(CO)_4$ at elevated temperatures. The problem with this method was that the 2031 cm^{-1} band of $Co_2(CO)_8$ was shown to gain considerable intensity at higher temperature due to changes in the isomeric composition of $Co_2(CO)_8$ [9], and hence the absorbance obtained for $HCo(CO)_4$ by difference proved to be inaccurate.

The analysis of $HCo(CO)_4$ in this work is based upon the highest-energy absorption band of this compound at 2116 cm^{-1}. Although its intensity is about 50-times lower than that of the strongest band at 2030 cm^{-1} [10], this choice is justified by the following advantages: (a) there is no overlap with bands of other cobalt carbonyl species, and (b) the overall cobalt concentration can be kept higher, corresponding well with the usual concentrations used in catalytic studies (in studies of the hydroformylation reaction the concentration of $HCo(CO)_4$ is a very important factor).

The quantitative analytical method was developed for systems with low CO pressure (0–30 atm.) and high H_2 pressure (up to 160 atm.). In these systems, the broad absorption band of the dissolved carbon monoxide in the 2100–2200 cm^{-1} region did not interfere, and the intensity of the sharp 2116 cm^{-1} band could be measured with the desired accuracy, especially with expanded spectra.

In order to quantitatively analyze the closed two-component ($Co_2(CO)_8 + Co_4(CO)_{12}$) and three-component ($Co_2(CO)_8 + Co_4(CO)_{12} + HCo(CO)_4$) systems, the absolute determination of the extinction coefficients of the bridging bands of the dicobalt and tetracobalt carbonyls, became essential. The calculation of the ϵ_3 value of the 2116 cm^{-1} analytical band of the cobalt carbonyl hydride was then performed in combination with the material balance of the mixed system.

Experimental

Preparation of Solutions of Tetracobalt Dodecacarbonyl for IR Measurements

0.402 g of fresh $Co_4(CO)_{12}$ crystals [11] were placed in a 250 ml measuring flask equipped with a two-neck joint. One opening was closed by a rubber stopper and the other connected to a vacuum line. The measuring flask was evacuated, and then connected through a thin stainless-steel tube to a solvent reservoir containing purified hexane and kept under N_2. Due to the pressure difference, the solvent flowed from the reservoir to the measuring flask up to the desired volume. Upon completion, the vacuum was disconnected, a magnetic bar was quickly placed in the flask and the latter was flushed with N_2. The solution was stirred for 20 min until all crystals were dissolved. A 10 ml syringe equipped with a long needle was introduced through the rubber stopper into the measuring flask, flushed several times with N_2 and then lowered into the solution. After filling it with 10 ml solution, the needle was removed and the syringe attached to the infrared cell through a special binding piece. The cell was flushed with the solution and then both its openings were tightly closed.

The spectra were recorded on a Perkin-Elmer Model 325 grating infrared spectrophotometer with tenfold wavenumber expansion. The scanning conditions were: gain = 360, suppression = 8, response = 3, scanning speed = 5–8 cm^{-1} min^{-1} and slit program = 4.5.

Parallelly, two other solutions containing 0.0186 g and 0.0165 g of $Co_4(CO)_{12}$ in 10 ml hexane each were prepared in the same way. The cell thickness in all measurements was 0.0194 cm.

Preparation of Solutions of Dicobalt Octacarbonyl for IR Measurements

0.2149 g, 0.2420 g and 0.2430 g of fresh $Co_2(CO)_8$ crystals [12] were placed in three 100 ml measuring flasks, each equipped with a two-neck joint. The flasks had been previously flushed for 30 min with CO and the crystals were introduced under CO stream. All operations and sampling procedures were similar to those described in the previous section except that they were performed under CO. The cell thickness in these experiments was 0.0205 cm.

The Indirect Method for the Determination of the Extinction Coefficient of $HCo(CO)_4$

1.3088 g $Co_2(CO)_8$ were dissolved in 655 ml hexane (pretreated with $LiAlH_4$ and distilled under N_2 atmosphere), to give a 5.84×10^{-3} mol/l solution. The solution was transferred into a 1093 ml stainless-steel autoclave by suction, with exclusion of air. The autoclave was equipped with an efficient stirrer and heated by means of a thermostated oil bath. The total pressure was measured with calibrated manometers.

A sampling tube reaching the bottom of the autoclave was connected to a flow-through type high pressure infrared cell [13]. Before each spectrum was scanned, the cell was flushed with 10–15 ml of fresh solution from the autoclave by opening a discharge valve placed after the cell. Total pressure was maintained constant in the whole system by simultaneously repressurizing the autoclave with hydrogen.

Spectra were scanned by a Perkin-Elmer Model 325 grating infrared spectrophotometer. The slit program was 4.5, corresponding to a spectral slit width of 0.87 cm^{-1} at 1900 cm^{-1}. Scanning speed was 5–8 cm^{-1} min^{-1}. Solvent absorption was compensated for by the use of a commercial variable path length cell. This variable cell also served as indicator for the cell thickness, which in this case was 0.028 cm at 38 ℃.

After the introduction of the solution into the autoclave, the system was pressurized with 8 atm. of CO, stirred and released to equilibrate with atmospheric pressure. The system was then pressurized with H_2 up to 100–105 atm. In this way, the initial partial pressure of CO in the system was ~0.6 atm. The temperature was adjusted to 43 ℃. The reaction time was 6 days. At least two spectra were recorded daily, and when three consecutive spectra were identical, the reaction was assumed to have reached equilibrium.

Results and Discussion

Principles of the Analytical Method

In the method developed in this work, it is assumed that at any moment all cobalt atoms in the system must exist in one of the three forms: $Co_4(CO)_{12}$, $Co_2(CO)_8$, and $HCo(CO)_4$. For this purpose CO and H_2 pressures were carefully selected to ensure the thermal stability of the carbonyls and their stability towards CO loss. Therefore, the difference between the sum of the concentrations of $Co_4(CO)_{12}$ and $Co_2(CO)_8$ and the initial concentration of the starting compound, must correspond to the concentration of the hydride.

The quantitative analysis was based upon the bridging CO stretching bands of the polynuclear carbonyls at 1858 (A_2) and 1867 (A_1) cm^{-1} and the terminal CO symmetric stretching band of $HCo(CO)_4$ at 2116 (A_3) cm^{-1}, clearly visible, isolated and sharp at low CO pressures (0–30 atm.).

Since both $Co_2(CO)_8$ and $Co_4(CO)_{12}$ have absorptions at 1858 and 1867 cm^{-1}, the actual bands will be due to a mixture of both compounds, as is the case for the two-component system [3]. The spectrum of the bridging region of a random mixture of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ is shown in Fig. 1.

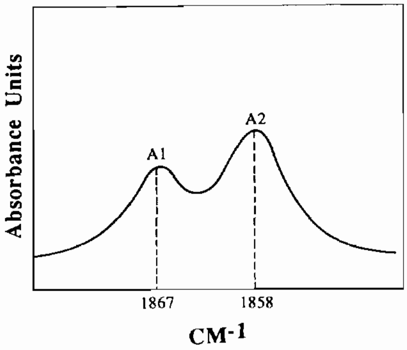

Fig. 1. The infrared spectrum of the bridging carbonyl region of a random mixture of $Co_2(CO)_8$ and $Co_4(CO)_{12}$. A_1 and A_2 are the measured intensities of the 1858 and 1867 cm^{-1} absorption bands.

According to Beer–Lambert's law [14], the following equations can be written

$$A_1 = b(\epsilon_{J1}C_1 + \epsilon_{K1}C_2) \qquad (1)$$

$$A_2 = b(\epsilon_{J2}C_1 + \epsilon_{K2}C_2) \qquad (2)$$

where $[J] = C_1 = [Co_4(CO)_{12}]$ and $[K] = C_2 = [Co_2(CO)_8]$ in mol/l units, b = cell thickness, and the ϵ values are the molar extinction coefficients, accordingly: $\epsilon_{J1} = \epsilon$ of $Co_4(CO)_{12}$ at 1867 cm^{-1}, $\epsilon_{J2} = \epsilon$ of $Co_4(CO)_{12}$ at 1858 cm^{-1}, $\epsilon_{K1} = \epsilon$ of $Co_2(CO)_8$ at 1867 cm^{-1} and $\epsilon_{K2} = \epsilon$ of $Co_2(CO)_8$ at 1858 cm^{-1}.

By subtracting eqn. (2) from eqn. (1), the following expressions are obtained

$$C_1 = \frac{\epsilon_{K2}A_1 - \epsilon_{K1}A_2}{b(\epsilon_{J1}\epsilon_{K2} - \epsilon_{J2}\epsilon_{K1})} \qquad (3)$$

$$C_2 = \frac{\epsilon_{J1}A_2 - \epsilon_{J2}A_1}{b(\epsilon_{J1}\epsilon_{K2} - \epsilon_{J2}\epsilon_{K1})} \qquad (4)$$

In order to simplify the equations and to avoid the use of the numerical values for all four extinction coefficients which would introduce a higher error, the ratios between the extinction coefficients found by Bor and Dietler were used [3, 4]. Since the starting compound in all the experiments carried out in this work was $Co_2(CO)_8$, ϵ_{K2} was chosen as the reference extinction coefficient, and hence the following ratios were obtained

$$\alpha = \frac{\epsilon_{J1}}{2\epsilon_{K2}} = 3.0125 \qquad \beta = \frac{\epsilon_{J2}}{2\epsilon_{K2}} = 0.1775$$

$$\gamma = \frac{\epsilon_{K1}}{\epsilon_{K2}} = 0.560$$

The α, β and γ are the measured values using the relative intensities during experiments in closed systems, taking into account the change in molarity by a factor of 2 when going from $Co_2(CO)_8$ to $Co_4(CO)_{12}$ or vice versa. The above values are based on the cobalt atom extinction ratios. The ratios which correspond to the molar extinction coefficients shall be defined as follows:

$$\alpha' = 2\alpha = 6.025 \qquad \beta' = 2\beta = 0.356$$

$$\gamma' = \gamma = 0.560$$

By substituting these values into eqns. (3) and (4), the following expressions for C_1 and C_2 are obtained

$$C_1 = \frac{0.172A_1 - 0.096A_2}{b\epsilon_{K2}} \tag{5}$$

$$C_2 = \frac{1.035A_2 - 0.061A_1}{b\epsilon_{K2}} \tag{6}$$

A_1 and A_2 are the measured intensities of the 1858 and 1867 cm^{-1} bands, as shown in Fig. 1, and the precise determination of the numerical value of ϵ_{K2} has been carried out and will be described in the next section.

In the closed two-component system containing only $Co_2(CO)_8$ and $Co_4(CO)_{12}$, the determination of the absolute concentration of both components becomes unnecessary, if the molar fraction of each component can be calculated. For example, in order to calculate the molar fraction of $Co_4(CO)_{12}$ in the reaction mixture, the following equation may be written

$$X_{(J)} = \frac{4C_1}{4C_1 + 2C_2} \tag{7}$$

By substituting eqns. (5) and (6) into eqn. (7) and by defining $Q = A_2/A_1$, the following relationship is obtained

$$X_{(J)} = \frac{0.409 - 0.232Q}{0.336 + Q} \tag{8}$$

This expression is very useful, since it does not require the knowledge of either the cell thickness or ϵ_{K2}, but only the ratio of the two analytical bands (Q). For the two-component system, the calculation of the molar fraction of one component (or both) would determine the system. In the case of a three-component system, where $HCo(CO)_4$ is present in addition to $Co_2(CO)_8$ and $Co_4(CO)_{12}$, the above considerations are no longer valid.

The concentration of $HCo(CO)_4$ (C_3) shall be obtained by subtracting the sum of the concentrations of $Co_4(CO)_{12}$ and $Co_2(CO)_8$ from the starting cobalt carbonyl concentration. Since the three compounds have different numbers of cobalt atoms, it is necessary to convert the molar concentrations to atom concentrations, according to the number of cobalt atoms that each compound contains. The $HCo(CO)_4$ concentration (C_3) will therefore be

$$C_3 = 2C_2^{(0)} - (2C_2 + 4C_1) \tag{9}$$

where $C_2^{(0)} = [Co_2(CO)_8]_{t=0}$

By substituting for C_1 and C_2 the following expression was obtained

$$C_3 = 2C_2^{(0)} - \frac{1.686A_2 - 0.566A_1}{b\epsilon_{K2}} \tag{10}$$

Therefore, the determination of the composition of the three-component system requires the knowledge of the cell thickness, the absolute concentration of the starting compound and ϵ_{K2}.

Determination of ϵ_{K2} and ϵ_{J1}

The only value for ϵ_{K2} existing in the literature is the one given by Noack [1]. However, this value, 2000 l mol^{-1} cm^{-1}, gave $C_2^{(0)}$ concentrations about 20% lower than expected from the amount of $Co_2(CO)_8$ initially charged into the system. Moreover, the intensity ratio of the 1867 and 1858 cm^{-1} bands (A_{1867}/A_{1858}) in Noack's paper was 0.6, to be compared with 0.560 (see eqn. for γ), which suggested that an impurity of $Co_4(CO)_{12}$ was present in the $Co_2(CO)_8$ solution measured. Since the maintenance of the material balance was a very important factor in the development of the quantitative analytical method presented here, the redetermination of ϵ_{K2} became essential.

The spectrum of a 6.285×10^{-3} mol/l solution of $Co_2(CO)_8$ in hexane is shown in Fig. 2a. The ratio between the intensities of the 1867 and 1858 cm^{-1} bands (A_{1867}/A_{1858}) was 0.559, which agrees well with the ratio of 0.560 expected for pure $Co_2(CO)_8$. The calculated extinction coefficient was $\epsilon_{K2} = 1735 \pm 20$ l mol^{-1} cm^{-1}.

Another experimental proof of the validity and accuracy of the ϵ_{K2} values, was the determination of the extinction coefficient of $Co_4(CO)_{12}$ at 1867 cm^{-1}, ϵ_{J1}. The ratio $2\epsilon_{K2}/\epsilon_{J1}$ should correspond to

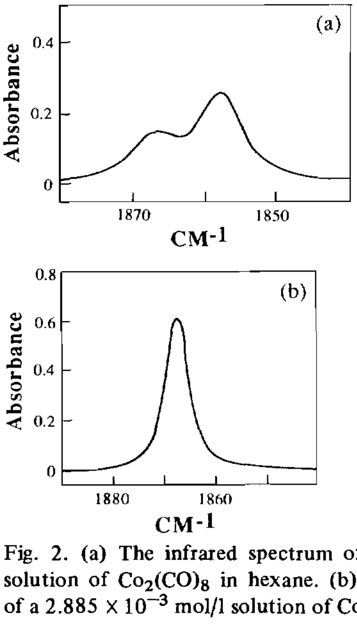

Fig. 2. (a) The infrared spectrum of a 6.285×10^{-3} mol/l solution of $Co_2(CO)_8$ in hexane. (b) The infrared spectrum of a 2.885×10^{-3} mol/l solution of $Co_4(CO)_{12}$ in hexane.

0.332, if the extinction coefficients have the correct value.

The spectrum of a 2.885×10^{-3} mol/l solution of $Co_4(CO)_{12}$ in hexane is shown in Fig. 2b. The calculated extinction coefficient was $\epsilon_{J1} = 10\,440 \pm 170$ l mol^{-1} cm^{-1}. The ratio of the two extinction coefficients was then checked

$$\frac{2\epsilon_{K2}}{\epsilon_{J1}} = \frac{3470}{10\,440} = 0.332 \qquad (11)$$

Temperature Dependence of the Extinction Coefficients

The ϵ_{K2} values for $Co_2(CO)_8$ were measured in hexane solutions at the working temperature of the spectrophotometer, *i.e.* ~40 °C. At this temperature, the bridged isomer (**I**) of $Co_2(CO)_8$, which gives rise to the 1867 and 1858 cm^{-1} bands, is present in abundance of 35.5% of the mixture of all three $Co_2(CO)_8$ isomers [9].

$$X_{(\mathrm{I})} = \left\{\frac{[\mathrm{I}]}{[\mathrm{I}] + [\mathrm{II}] + [\mathrm{III}]}\right\} 100 = 35.5\% \qquad (12)$$

This means that the extinction coefficient is directly dependent on the abundance of the bridged isomer. In this case, the 'true' ϵ_{K2}, $\epsilon_{K2}^{(\mathrm{tot})}$, corresponding to an extrapolated 100% theoretical abundance of the bridged isomer, will be

$$\epsilon_{K2}^{(\mathrm{tot})} = \epsilon_{K2}^{(\mathrm{obs})} 100/X_{(\mathrm{I})} \qquad (13)$$

This relationship implies that while $\epsilon_{K2}^{(\mathrm{obs})}$ is a function of $X_{(\mathrm{I})}$, $\epsilon_{K2}^{(\mathrm{tot})}$ is constant. When temperature changes, $\epsilon_{K2}^{(\mathrm{tot})}$ may be regarded at first approximation as being independent of temperature. In the gas phase, $\epsilon_{K2}^{(\mathrm{tot})}$ is to some extent a function of temperature, since temperature affects the rotation modes and the harmonicity of the vibrational modes [15–18]. In solution, however, the rotational transitions are 'frozen in', and if there would be some other type of influence it would be negligible, at least within the temperature range that has been used throughout this work. On the other hand, $\epsilon_{K2}^{(\mathrm{obs})}$ will indirectly be dependent on temperature

$$\epsilon_{K2}^{(\mathrm{obs})} = f\{X_{(\mathrm{I})}\} \text{ and } X_{(\mathrm{I})} = f\{-T\} \qquad (14)$$

$\epsilon_{K2}^{(\mathrm{obs})}$ is a function of the abundance of isomer **I**, and the latter is an inverse function of the temperature. The dependence of $X_{(\mathrm{I})}$ on temperature is shown in Fig. 3. Within a narrow range of temperatures it is reasonable to write the following relationship

$$\epsilon_{K2(b)}^{(\mathrm{obs})} = \epsilon_{K2(a)}^{(\mathrm{obs})} \frac{X_{(\mathrm{I})(b)}}{X_{(\mathrm{I})(a)}} \qquad (15)$$

where *a* and *b* are two consecutive temperatures for which the extinction coefficient is calculated. The calculated $\epsilon_{K2}^{(\mathrm{obs})}$ values for several temperatures are shown in Table I. However, these values do not include a possible contribution from the narrower (and hence at the band maximum more intensive) band shape due to the lower temperature.

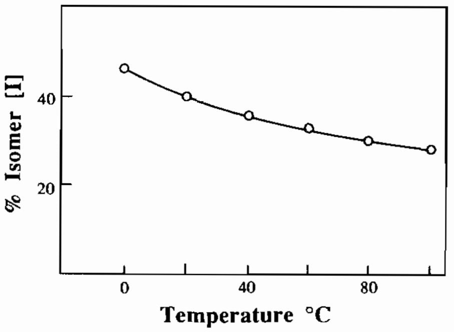

Fig. 3. The abundance (mole fraction) of the bridging isomer of $Co_2(CO)_8$ (I), as a function of temperature.

TABLE I. The Calculated $\epsilon_{K2}^{(\mathrm{obs})}$ Values of the 1858 cm^{-1} Band of $Co_2(CO)_8$ for Several Temperatures

T (°C)	Isomer I (%)	$\epsilon_{K2(T)}^{(\mathrm{obs})}$ (l mol^{-1} cm^{-1})
43	35.5	1735
30	38.0	1857
22	40.0	1954
5	44.0	2150
−5	47.5	2321
−10	49.0	2394
−20	52.0	2540

Extrapolation of the molecular extinction coefficient of $Co_2(CO)_8$ for the pure bridged form gives a value of 4890 ± 55 l mol^{-1} cm^{-1} at ~40 °C.

Indirect Determination of the Extinction Coefficient of $HCo(CO)_4$ at 2116 cm^{-1}

An example of a typical experiment carried out for the determination of the extinction coefficient of $HCo(CO)_4$ at 2116 cm^{-1} is summarized in Table II. The concentrations of $HCo(CO)_4$ for each intensity were calculated using the three-component system method which has been described previously. Then, the different intensities of the 2116 cm^{-1} band were plotted as function of the calculated $HCo(CO)_4$ concentrations, and the slope of the line shown in Fig. 4 directly yielded the value of the extinction coefficient.

In order to determine precisely the extinction coefficient of $HCo(CO)_4$ at 2116 cm^{-1}, 33 data points resulting from 33 similar experiments were collected. A straight line was fitted through all the points by means of an adequate computer program, and the value obtained was $\epsilon_3 = 330 \pm 10$ l mol^{-1} cm^{-1}.

TABLE II. The Measured Infrared Intensities for the 2116, 1867 and 1858 cm^{-1} Carbonyl Bands and the Calculated Concentrations for $HCo(CO)_4$, $Co_2(CO)_8$ and $Co_4(CO)_{12}$

Time (h)	A_{1867}	A_{1858}	A_{2116}	$Co_4(CO)_{12}$ [a] (mol/l)	$Co_2(CO)_8$ [a] (mol/l)	$HCo(CO)_4$ (mol/l)
0	0.177	0.317		0.00002	0.0118	0
9	0.162	0.290	0.014	0.00001	0.0108	0.0014
22	0.138	0.247	0.029	0.00001	0.0092	0.0028
46	0.112	0.201	0.051	0.00001	0.0075	0.0046
68	0.087	0.156	0.065	0.00001	0.0058	0.0060
102	0.070	0.123	0.077	0.00001	0.0046	0.0074
143	0.068	0.121	0.080	0.00001	0.0045	0.0076

$p(H_2)$ = 100 atm. [a]Calculated with respect to cobalt atoms.

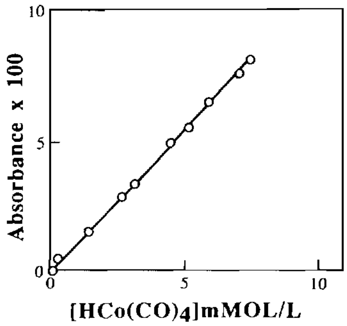

Fig. 4. The intensities of the 2116 cm^{-1} infrared absorption band of the cobalt carbonyl hydride as a function of its calculated concentrations.

The analytical method described here, in which measured band intensities and the material balance are precisely monitored, may be further utilized to determine the concentrations of additional cobalt carbonyl species commonly encountered during the hydroformylation reaction.

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