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FUNDAMENTAL METAL CARBONYL EQUILIBRIA.

II *. A QUANTITATIVE STUDY OF THE EQUILIBRIUM BETWEEN DIRHODIUM OCTACARBONYL AND TETRARHODIUM DODECACARBONYL UNDER CARBON MONOXIDE PRESSURE

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Summary

The reversible reaction of $Rh_4(CO)_{12}$ with carbon monoxide under pressure to yield thermally unstable $Rh_2(CO)_8$ has been studied by high-pressure infrared spectroscopy. The equilibrium constant and the thermodynamic parameters of this reaction have been determined in the temperature range $+30$ to -30°C, at 100 to 200 bar CO pressure with n-hexane as solvent: ΔH^0 45.5 ± 1.3 kJ mol^{-1}, ΔS^0 266.6 ± 4.7 J mol^{-1} K^{-1}. A detailed comparison with the analogous cobalt carbonyl system is presented. Preliminary kinetic measurements show that the rate of the cluster-breaking reaction for $Rh_4(CO)_{12}$ with CO at -22°C is ca. 500-times faster than that for the corresponding cobalt cluster.

Introduction

Although the equilibrium between dicobalt octacarbonyl, tetracobalt dodecacarbonyl and carbon monoxide (eq. 1) was studied in 1954 [1], and a recent

$$2Co_2(CO)_8 \rightleftarrows Co_4(CO)_{12} + 4CO \qquad (1)$$

redetermination proved [2] that those results were very accurate, no quantitative information has been reported for the analogous equilibrium for the rhodium carbonyls (eq. 2).

$$2Rh_2(CO)_8 \rightleftarrows Rh_4(CO)_{12} + 4CO \qquad (2)$$

This lack of data is all the more to be regretted since industrially several million

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[*] For Part I see [2].

[**] The results described form part of the planned dissertation of F.O., ETH Zurich.

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tons of aldehydes per year are produced by the oxo-process from olefins with carbon monoxide and hydrogen. The most frequently used homogeneous catalysts of this reaction are the carbonyls of cobalt and rhodium [3]. More precise fundamental knowledge on the transformations of these carbonyls is desirable for a better understanding of these catalytic systems, especially in view of the considerable and characteristic differences between the oxo-synthesis (hydroformylation) performed with cobalt or rhodium carbonyl catalysts [4].

The absence of quantitative equilibrium data for rhodium carbonyls is clearly attributable to the extreme thermal instability of $Rh_2(CO)_8$.

Although Hieber and Lagally reported in 1943, inter alia, a rhodium carbonyl formulated as $Rh_2(CO)_8$ [5], several laboratories were unsuccessful in reproducing this result [6–8]. It was only in 1972 that Whyman observed that in the IR spectrum of $Rh_4(CO)_{12}$ under high carbon monoxide pressure at subzero temperatures there appeared new IR absorption bands which, by analogy to those of the bridged form of $Co_2(CO)_8$ [9], he assigned to $Rh_2(CO)_8$ [10]. Unfortunately no equilibrium constants and/or thermodynamic parameters of reaction 2 could be calculated from Whyman's spectra for two reasons:

(i) the simple routine spectrometer he used did not give satisfactory information on band intensity values, and thus could not be used for quantitative analysis of the concentrations, and

(ii) because liquid paraffin-heptane mixture was used as solvent, it was not possible to make a reasonable estimate of the concentration of dissolved carbon monoxide.

Besides the industrial interest already mentioned, a study of equilibrium 2 seemed to be challenging also from the point of view of theoretical considerations in the light of the following prediction by Chini and Heaton [11]: "Very similar reactions such as eq. 2 in which the variation in entropy is practically identical to that in eq. 1, have very different equilibrium constants. This shows that in this case (i.e. for reaction 2) ΔH^0 must be much less positive".

With the aim of filling this gap in the thermodynamic information we have quantitatively analysed reaction 2 using our high-pressure IR equipment [12]. We used n-hexane as solvent, as in our previous spectroscopic [9e,13], thermodynamic and kinetic studies [2,14], in order to allow a comparison between the related cobalt and rhodium carbonyl systems.

Results and discussion

IR spectra

Figure 1 shows the C–O stretching region of a spectrum of typical quality, of a $Rh_4(CO)_{12}$ solution in n-hexane (d 0.57 mm, c 9.6×10^{-4} mol dm^{-3}) under 198 bar carbon monoxide at 19.5°C. The characteristic bridging bands at 1862 and 1847 cm^{-1}, ascribed to $Rh_2(CO)_8$ by Whyman [10], appear in the spectrum even at this "high" temperature, in contrast to his observation.

We explain this difference in terms of the different solubilities of carbon monoxide in the solvents used. Whyman usually used high-boiling paraffin-oils (or, as in this case, a mixture of these with lighter hydrocarbons), which are much poorer solvents for gases than the hexane we used. The apparent motive of Whyman [15] was to reduce the interference by the broad absorption band of dissolved carbon

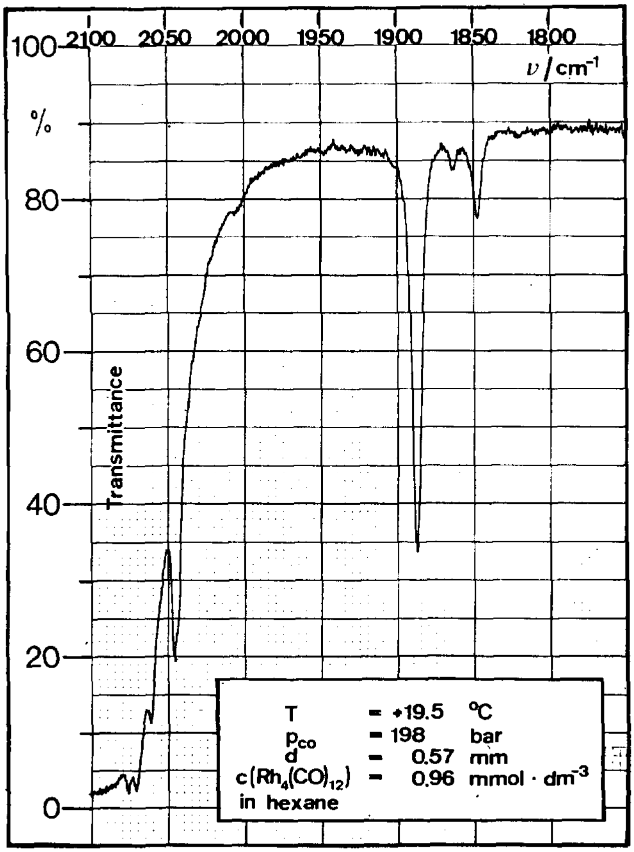

Fig. 1. "Routine" spectrum of $Rh_4(CO)_{12}$ in hexane (d 0.57 mm, c 9.6×10^{-4} mol dm^{-3}) under 198 bar carbon monoxide pressure, at +19.5°C.

monoxide but this is a self-defeating approach in the cases where carbon monoxide is a reaction partner: obviously it is the concentration of dissolved CO which counts, and much higher pressures are needed to achieve the same degree of reaction reached at lower pressures with low molecular weight alkanes as solvents. As Luther and Hiemenz showed [16], the solubility of carbon monoxide in alkanes is approximately constant if it is expressed in molar fractions, i.e. $x_{CO} = 1.8\ (\pm 0.1) \times 10^{-3}$. We chose n-hexane as a compromise between a low molecular weight and a relatively low volatility at room temperature.

As Fig. 1 shows, strong interference by dissolved carbon monoxide in the terminal region is inevitable with the high carbon monoxide concentrations (ca. 2.5 mol dm^{-3} at the maximum) needed. (As a consequence the systems with metal carbonyls which do not possess bridging carbonyl ligands are much more difficult to analyze and the results are less accurate. It is hoped that with digitalized data processing instruments, much progress will be possible even for these cases).

Figure 2 shows examples of the spectra as they were scanned, with wave number expansion and low scanning speed, for the precise quantitative analyses. A slight low-energy shift of the absorption maxima was observed at lower temperatures.

In Fig. 3 we present a spectrum of a solution which was first equilibrated at 198 bar carbon monoxide pressure and at −45°C, with the carbon monoxide pressure

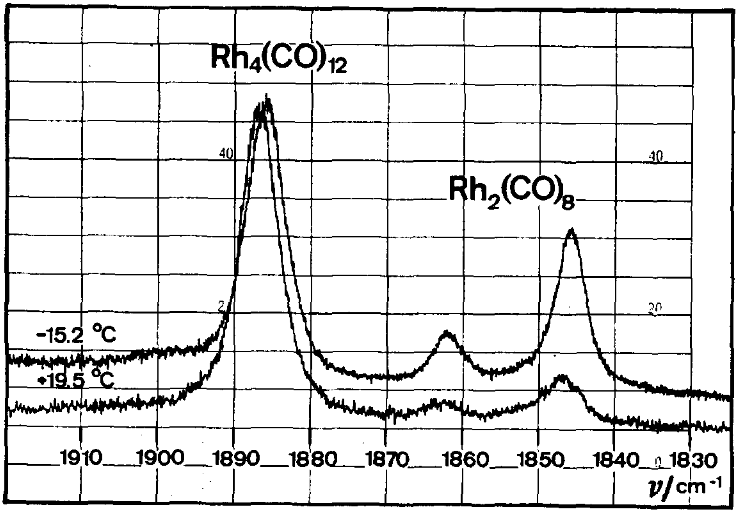

Fig. 2. Expanded spectra of $Rh_4(CO)_{12}$ and $Rh_2(CO)_8$ equilibrium mixtures, as used for obtaining the analytical data of Tables 1, 2, 4 and 5 (in absorbance). Carbon monoxide pressure: 198 bar, temperatures as indicated.

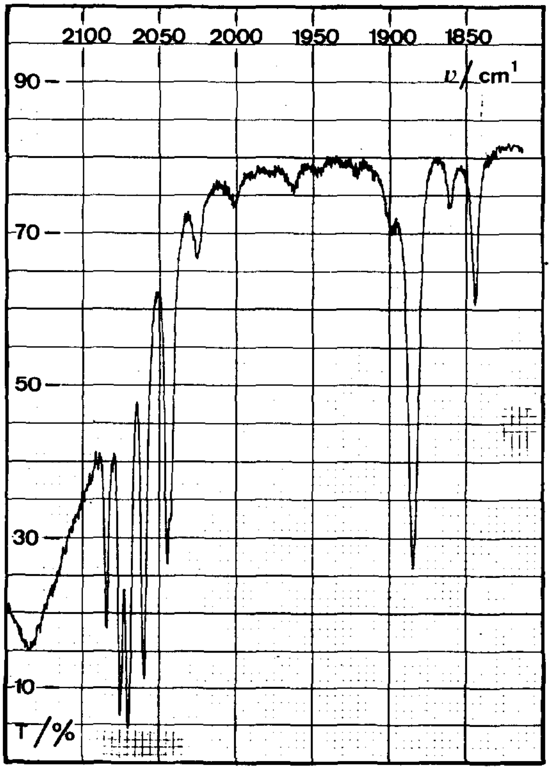

Fig. 3. Spectrum of a sample of $Rh_4(CO)_{12}$ in hexane equilibrated under 198 bar carbon monoxide pressure at −45°C. The pressure was reduced to 20 bar immediately before scanning, to reduce the intensity of the absorption caused by dissolved carbon monoxide.

then reduced to only 20 bar, and the spectrum recorded quickly thereafter. In this way we reduced considerably the strong interference by the high concentration of dissolved carbon monoxide. In this way we were also able to observe the absorption bands associated with the terminal C–O stretching vibrations. In addition to the bands of $Rh_4(CO)_{12}$ at 2075, 2070 and 2045 cm^{-1} we saw two new strong bands at 2084 and 2060 cm^{-1}, which we attribute to $Rh_2(CO)_8$, as did Whyman [10].

The thermodynamic parameters of the equilibrium

The observed absorbance values for the analytical bands, as well as the concentrations calculated for them (by applying the corrections mentioned in the experimental part) are given in Tables 1 and 2. The equilibrium constants K'_p and K_c are shown in

TABLE 1

QUANTITATIVE EVALUATION OF THE IR SPECTRA OF EQUILIBRIUM MIXTURES OF $Rh_4(CO)_{12}$ AND $Rh_2(CO)_8$ UNDER 198 BAR CARBON MONOXIDE PRESSURE IN HEXANE ($c_0(Rh_4(CO)_{12})$ 9.597×10^{-4} mol dm^{-3}, cell thickness d 0.585 mm (at 0°C))

T (°C)	Correction factor $\gamma(T)$ [a]	Reduced absorbance $E(0°C)=\gamma(T)\times E(T)$			$Rh_2(CO)_8$	
		$Rh_4(CO)_{12}$ 1886 cm^{-1}	$Rh_2(CO)_8$ 1863 cm^{-1}	$Rh_2(CO)_8$ 1847 cm^{-1}	$\frac{E(1847\ cm^{-1})}{E(1863\ cm^{-1})}$ [b]	d [c] (mm)
−43.0	0.8348	0.2112	0.1160	0.3402	2.93	0.597
−21.5	0.9100	0.2866	0.0801	0.2425	3.03	0.583
−21.5	0.9100	0.2753	0.0828	0.2525	3.05	0.581
−20.0	0.9157	0.2839	0.0733	0.2244	3.07	0.562
−19.5	0.9177	0.3056	0.0711	0.2212	3.11	0.583
−15.2	0.9346	0.3238	0.0631	0.1869	2.96	0.569
−15.3	0.9342	0.3270	0.0617	0.1910	3.10	0.578
−15.5	0.9334	0.3267	0.0569	0.1811	3.18	0.566
−10.5	0.9539	0.3529	0.0677	0.1898	2.80	0.606
−10.2	0.9552	0.3558	0.0654	0.1929	2.95	0.612
−5.9	0.9736	0.3768	0.0565	0.1679	2.98	0.611
−0.6	0.9972	0.3740	0.0424	0.1247	2.94	0.563
−0.5	0.9977	0.3986	0.0354	0.1197	3.38	0.586
4.0	1.0188	0.3999	0.0321	0.1034	3.22	0.571
4.6	1.0216	0.4204	0.0332	0.1119	3.37	0.603
11.6	1.0564	0.4358	0.0264	0.0872	3.30	0.596
11.6	1.0564	0.4426	0.0275	0.0872	3.17	0.603
11.4	1.0554	0.4311	0.0306	0.0865	2.83	0.589
19.5	1.0986	0.4614	0.0198	0.0626	3.16	0.600
19.6	1.0991	0.4342	0.0220	0.0654	2.98	0.571
19.6	1.0991	0.4331	0.0192	0.0632	3.29	0.568

[a] The determination of this correction factor is described in the experimental section. $\gamma(T)=(1+\beta T)^{-1}$, $\beta=(-4.602\pm0.070)\times10^{-3}$ $°C^{-1}$. [b] For the interpretation of the constancy of this ratio E (1847 cm^{-1})/E(1863 cm^{-1}) = 3.09 ± 0.17 see text. [c] Further control of the cell thickness using the following relationship: $d=(E_2\varepsilon_4+2E_4\varepsilon_2)(1+0.001\times p_{co})/\varepsilon_2\times\varepsilon_4\times2c_0$; $d=0.585\pm0.016$ mm (Here subscripts 2 refer to the band at 1847 cm^{-1} of $Rh_2(CO)_8$ and 4 to the band at 1886 cm^{-1} of $Rh_4(CO)_{12}$; for the numerical ε_i values see the experimental section.).

Table 2. The constants are defined as follows:

$$K_p' = \frac{[Rh_4(CO)_{12}] \times p_{CO}^4}{[Rh_2(CO)_8]^2} \tag{3}$$

$$K_c = \frac{[Rh_4(CO)_{12}] \times [CO]^4}{[Rh_2(CO)_8]^2} \tag{4}$$

The two constants are related by $K_c = K_p'\alpha^4$, where α is the solubility of carbon monoxide in hexane: $\alpha = 0.012$ mol bar^{-1} (c.f. comment in ref. [14]).

The following relationships were found for the temperature dependence of the equilibrium constants:

$$\ln K_p' = 49.75 - 5474 \times 1/T \tag{5}$$

$$\ln K_c = 32.06 - 5474 \times 1/T \tag{6}$$

The dimensionless thermodynamic equilibrium constant K_{th} where the concentrations are expressed in terms of molar fractions, can be obtained by the following equation:

$$K_{th} = \frac{[Rh_4(CO)_{12}] \times [CO]^4}{[Rh_2(CO)_8]^2} \times \frac{1}{(\delta_{solv}/M_{solv} + \alpha p_{CO})^3} \tag{7}$$

With hexane as solvent, we obtained with $\delta_{solv}/M_{solv} = 7.66$ mol dm^{-3} the following

TABLE 2

EXPERIMENTAL VALUES OF THE EQUILIBRIUM CONSTANTS AT VARIOUS TEMPERATURES AND AT 198 BAR CARBON MONOXIDE PRESSURE IN HEXANE

T (°C)	$[Rh_4(CO)_{12}]$ [a] (10^{-3} mol dm^{-3})	$[Rh_2(CO)_8]$ [a] (10^{-3} mol dm^{-3})	$\ln K_p'$ [b]	$\ln K_c$ [c]
−21.5	0.4553	0.6896	28.01	10.32
−21.5	0.4374	0.7170	27.89	10.20
−20.0	0.4510	0.6372	28.15	10.46
−19.5	0.4855	0.6281	28.26	10.56
−15.2	0.5144	0.5307	28.65	10.96
−15.3	0.5195	0.5424	28.62	10.93
−15.5	0.5190	0.5142	28.72	11.03
−10.5	0.5606	0.5389	28.71	11.02
−10.2	0.5653	0.5478	28.68	10.99
−5.9	0.5986	0.4768	29.02	11.33
−0.6	0.5942	0.3541	29.60	11.91
−0.5	0.6332	0.3399	29.75	12.06
4.0	0.6353	0.2936	30.05	12.35
4.6	0.6679	0.3177	29.94	12.25
11.6	0.6923	0.2476	30.47	12.78
11.6	0.7031	0.2476	30.49	12.80
11.4	0.6849	0.2456	30.48	12.79
19.5	0.7330	0.1778	31.19	13.50
19.6	0.6898	0.1857	31.04	13.35
19.6	0.6881	0.1795	31.11	13.42

[a] $c_i = E_i/\varepsilon_i \times d$. [b] See eq. 3. [c] See eq. 4.

TABLE 3

COMPARISON OF THE THERMODYNAMIC PARAMETERS OF THE TWO ANALOGOUS REACTIONS OF COBALT [2] AND RHODIUM: $2M_2(CO)_8 \underset{\text{in hexane}}{\overset{K_c, K'_p}{\rightleftarrows}} M_4(CO)_{12} + 4CO$

M	$K_c = \frac{[M_4(CO)_{12}][CO]^4}{[M_2(CO)_8]^2}$ (mol^3 dm^{-9})		$K'_p = \frac{[M_4(CO)_{12}] \times p^4_{CO}}{[M_2(CO)_8]^2}$ (dm^3 × bar^4 mol^{-1})	
	$\Delta H^{0\,a}$	$\Delta S^{0\,b}$	$\Delta H^{0\,a}_p$	$\Delta S^{0\,b}_p$
Co	29.5 ± 0.5 123.5 ± 2.1	64.7 ± 1.3 270.9 ± 5.4	29.5 ± 0.5 123.5 ± 2.1	99.8 ± 1.3 417.8 ± 5.4
Rh	10.9 ± 0.3 45.5 ± 1.3	63.7 ± 1.1 266.6 ± 4.7	10.9 ± 0.3 45.5 ± 1.3	98.9 ± 1.1 413.6 ± 4.7

[a] In kcal mol^{-1} (upper values) and kJ mol^{-1} (lower values). [b] In cal mol^{-1} K^{-1} (upper values) and J mol^{-1} K^{-1} (lower values).

expression:

$$\ln K_{th} = 32.06 - 3\ln(7.66 + 0.012\,p_{CO}) - 5474 \times 1/T \qquad (8)$$

However, for the practical use of our results in the homogeneous catalysis, the values of K_c and especially of K'_p, seem to be more useful.

The ΔH^0 and ΔS^0 values calculated for the temperature range +20 to −20°C are listed in Table 3, with the corresponding values for the analogous cobalt system being included for comparison *. Both the less positive ΔH^0 value and the equality of the reaction entropies were qualitatively predicted by Chini and Heaton [11].

The ΔG^0_{298} values of both reactions are shown graphically in Fig. 4. The thermal instability of $Rh_2(CO)_8$ (under 1 bar of CO pressure), a constrast with the behaviour of $Co_2(CO)_8$, is clearly evidenced by this plot.

The explanation of this highly varying stability can be given in terms of the bond enthalpy contributions: the metal–metal bond enthalpy increases more on going from cobalt to rhodium than does the metal–CO bond enthalpy. New bond enthalpy values for the Co and Rh carbonyls which we recently calculated will be presented and discussed elsewhere [18].

The equilibrium concentrations vs. CO pressure and temperature are illustrated in two different types of plot (Fig. 5 and 6). Figure 5 is a type of "phase diagram": it shows the stability regions of the single carbonyls in a p_{CO}-T^{-1} field. The lines connect p_{CO}-T combinations which correspond to equal octacarbonyl/dodecacarbonyl ratios. This "phase diagram" is evidently valid only for hexane solutions; for other solvents the ordinate (reflecting the solubility of CO gas) must be shifted to correspond to the different gas solubilities. Also, the absolute concentration influences the position of the iso-concentration lines. The plot presented is for solutions initially millimolar in the dodecacarbonyls, i.e. 0.004 molar in g-atom metal.

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* The entropy of reaction for the cobalt system was reported earlier [2] as ΔS^0 135 cal mol^{-1} K^{-1}. This value is in error, owing to a sign error in eq. 10 of ref. [2].

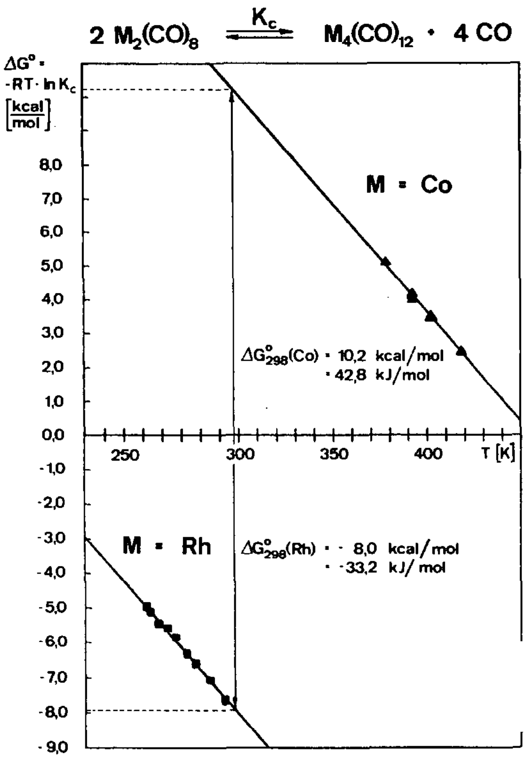

Fig. 4. Graphical comparison of the ΔG^0 vs. T changes for the cobalt and rhodium systems.

The curves in Fig. 6 are the usual complex equilibrium lines. However, we know of no previous example in which the behaviour of complexes having a ligand which is gaseous in the free state have been represented in this way. The scale of the abscisse is again $\log p_{CO}$; consequently the plot is again valid for hexane solutions only. The curves are isotherms, as indicated, and the concentration is the same as for Fig. 5. The computer procedure which is the basis for this computer plot solves the equilibrium equation in terms of the relative octacarbonyl concentration (y), which can be expressed as followed:

$$\frac{K'_p \times a}{p_{CO}^4} \times y^2 + y - 1 = 0 \tag{9}$$

where

$$a = 2[M_2(CO)_8] + 4[M_4(CO)_{12}] \tag{10}$$

and

$$y = 2[M_2(CO)_8]/a \tag{11}$$

Experimental proof of the stoichiometry of the reaction

Although we (like Whyman [10]) had no doubts concerning the identity of the species to which the bridging C–O stretching bands at 1862 and 1847 cm^{-1} belong, it seemed desirable to confirm the stoichiometry of the reaction by experiment.

For the following general reaction:

$$2\,Rh_2(CO)_u \rightleftarrows Rh_4(CO)_{12} + v\,CO \tag{12}$$

where $u = (12 + v)/2$

the formula for the equilibrium constant K'_p (eq. 3) has been expressed in terms of v

$$v = \ln\left(\frac{K'_p[Rh_2(CO)_u]^2}{[Rh_4(CO)_{12}]}\right)/\ln p_{CO} \tag{13}$$

The average for v in the two series of experiments at 148 bar (see Table 4) and 98 bar (see Table 5) is 3.97 ± 0.07. The stoichiometry predicted by Whyman [10] is exactly verified.

Semiquantitative kinetic observations

To our surprise the equilibrium compositions were reached after relatively very short periods, even at quite low temperatures. To provide at least preliminary data about the rate of the reaction, the concentration vs. time curves were studied at −22°C at 220 bar (Fig. 7) and (less reliably) 100 bar carbon monoxide pressures, starting from equilibrated solutions at +27°C under the indicated carbon monoxide pressures. The very high reaction rate prevented our obtaining IR spectra as good as those for the equilibrium measurements, since our spectrometer is of the classical dispersion type with grating. Hence, the concentration values show a considerably higher scatter (or considerably less precision) than those for the equilibrium study.

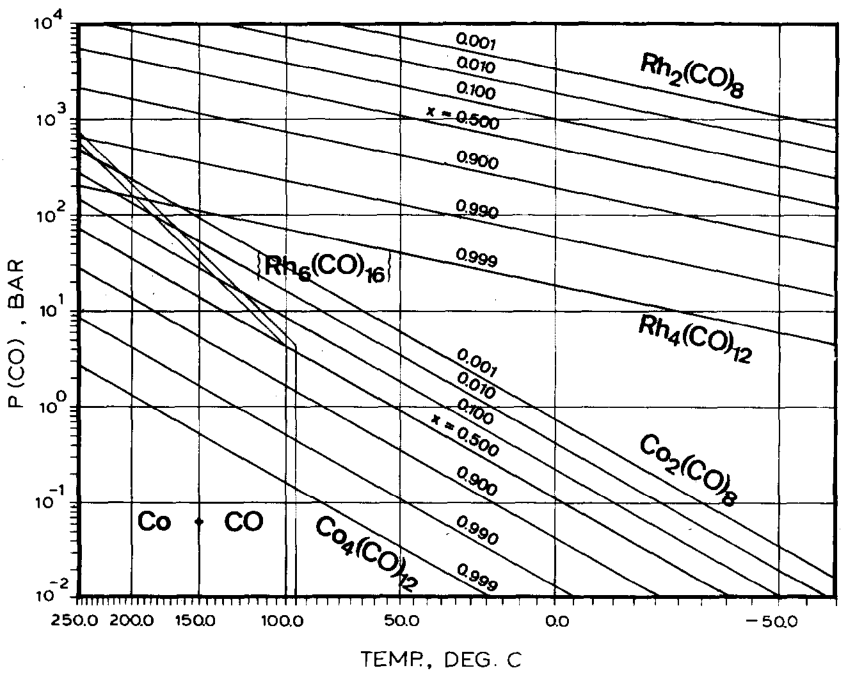

Fig. 5. Equilibrium compositions as a function of temperature and carbon monoxide pressure, in hexane (total metal concentration: 0.004 mol dm^{-3}, curve parameter $x = 1 - y$; for y see eq. 11). The indication of the region of the stability of $Rh_6(CO)_{16}$ is only tentative. The double line at 100°C indicates the thermal stability limit of cobalt carbonyls: for details see p. 300 of ref. 2.

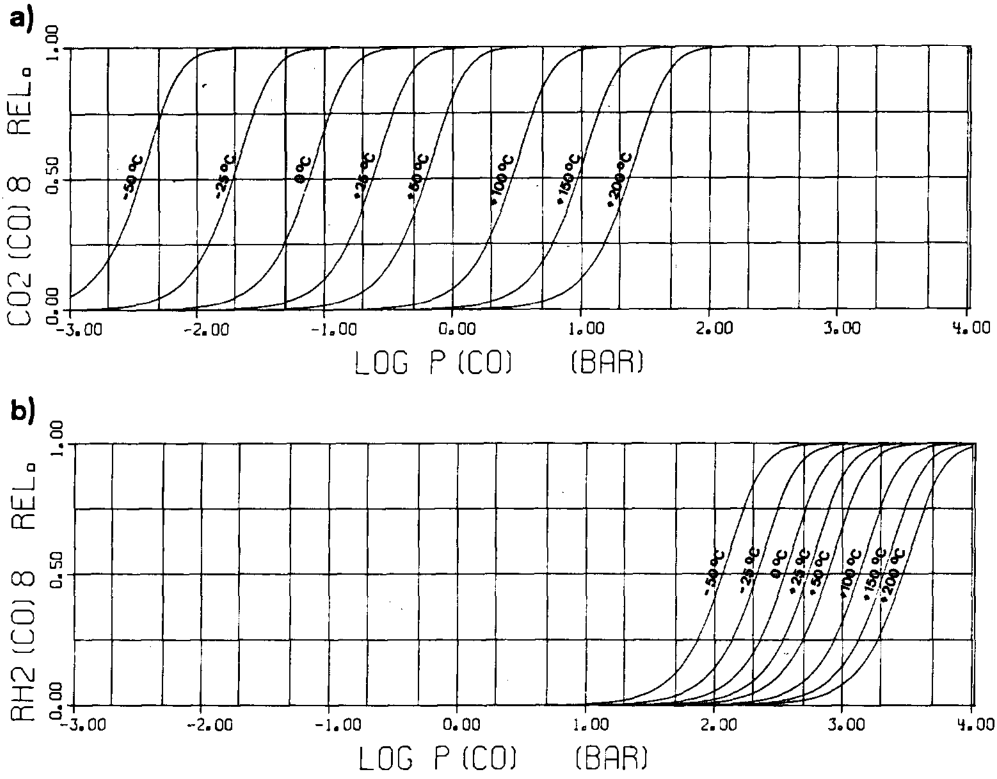

Fig. 6. Graphical comparison of the $2M_2(CO)_8 \rightleftarrows M_4(CO)_{12} + 4CO$ equilibria for (a) M = Co and (b) M = Rh, in rel. $[M_2(CO)_8]$ (corresponding to the value y in eq. 11) vs. $\log p_{CO}$. The curves (isotherms) refer to the same series of the temperature as indicated.

Evenso the following conclusions could be reached unequivocally:

(a) the reaction is first order in $Rh_4(CO)_{12}$ (as in the cobalt case [14]);

(b) although the 100 bar series yielded quite poor quality results a first order dependence on p_{CO} is very likely (best fit order: 0.7 ± 0.3);

(in the same temperature region the analogous cobalt reaction was second order in p_{CO}, and the first order region was reached only at temperatures above 125°C [14]);

(c) the half-life time of the reaction at −22°C and under 200 bar of CO pressure is $\tau_{1/2} = 16.0 \pm 0.4$ min ($k_{obs} = 0.0164$ dm^3 mol^{-1} min^{-1}); this is about 500 times faster (490 ± 12) than the analogous reaction of $Co_4(CO)_{12}$ under the same conditions!

Without more detailed kinetic studies (to be performed with a faster system, e.g. FT-IR) it would be unwise to attempt to offer an explanation for this difference in the behaviour of the two analogous systems.

Experimental

Chemicals

High purity carbon-monoxide was prepared by catalytic dehydrogenation of formic acid at 280°C, washed with aqueous potassium hydroxide solution to

TABLE 4

QUANTITATIVE EVALUATION OF THE IR SPECTRA OF EQUILIBRIUM MIXTURES OF $Rh_4(CO)_{12}$ AND $Rh_2(CO)_8$ UNDER 148 BAR CARBON MONOXIDE PRESSURE IN HEXANE. ($c_0(Rh_4(CO)_{12}) = 1.371 \times 10^{-3}$ mol dm^{-3}; $d = 0.567$ mm (at 0°C))

T (°C)	Correction factor $\gamma(T)$ [a]	Reduced absorbance (0°C) $E(0°C) = \gamma(T) \times E(T)$			d [b] (mm)	v [c]
		$Rh_4(CO)_{12}$ 1886 cm^{-1}	$Rh_2(CO)_8$ 1863 cm^{-1}	$Rh_2(CO)_8$ 1847 cm^{-1}		
−31.0	0.8751	0.3719	0.0613	0.1925		3.86
−28.8	0.8830	0.3444	0.0675	0.1987		3.92
−24.9	0.8972	0.3993	0.0574	0.1682		3.90
−20.0	0.9157	0.5655	0.0595	0.1763	0.563	3.93
−20.0	0.9157	0.5449	0.0641	0.1786	0.548	3.95
−10.1	0.9556	0.5939	0.0463	0.1338	0.555	3.98
−10.1	0.9556	0.6068	0.0468	0.1362	0.567	3.98
−4.8	0.9784	0.5870	0.0416	0.1101	0.533	3.98
−5.0	0.9775	0.5963	0.0391	0.1075	0.539	3.97
0.0	1.0000	0.6520	0.0285	0.0800	0.563	3.91
0.0	1.0000	0.6650	0.0250	0.0760	0.570	3.88
10.0	1.0482	0.7049	0.0173	0.0524	0.585	3.86
10.0	1.0482	0.7128	0.0194	0.0550	0.568	3.88
19.2	1.0969	0.7031	0.0137	0.0428	0.577	3.90
19.2	1.0969	0.7075	0.0137	0.0411	0.579	3.89
30.0	1.1602	0.7234	0.0104	0.0377	0.589	3.98
30.0	1.1602	0.7338	0.0116	0.0383	0.598	3.98

[a] See Table 1. [b] See Table 1; $d = 0.567 \pm 0.019$ mm. [c] $v = \ln(K'_p \times [Rh_2(CO)_8]^2/[Rh_4(CO)_{12}])/\ln p_{co}$.

TABLE 5

QUANTITATIVE EVALUATION OF THE IR SPECTRA OF EQUILIBRIUM MIXTURES OF $Rh_4(CO)_{12}$ AND $Rh_2(CO)_8$ UNDER 98 BAR CARBON MONOXIDE ($c_0(Rh_4(CO)_{12} = 1.371 \times 10^{-3}$ mol dm^{-3}; cell thickness $d = 0.540$ mm (at 0°C))

T (°C)	Correction factor $\gamma(T)$ [a]	Reduced absorbance (0°C) $E(0°C) = \gamma(T) \times E(T)$			d [b] (mm)	v [c]
		$Rh_4(CO)_{12}$ 1886 cm^{-1}	$Rh_2(CO)_8$ 1863 cm^{-1}	$Rh_2(CO)_8$ 1847 cm^{-1}		
−30.0	0.8787	0.5448	0.0492	0.1406	0.499	4.01
−30.0	0.8787	0.5514	0.0483	0.1362	0.501	4.00
−20.0	0.9157	0.6236	0.0385	0.1090	0.537	4.07
−20.0	0.9157	0.6273	0.0389	0.1071	0.538	4.06
−10.4	0.9543	0.6532	0.0262	0.0754	0.536	4.07
−10.4	0.9543	0.6494	0.0262	0.0730	0.532	4.06
0.0	1.0000	0.6875	0.0190	0.0545	0.548	4.09
0.0	1.0000	0.6840	0.0175	0.0525	0.544	4.07
10.0	1.0482	0.7285	0.0105	0.0314	0.563	3.99
10.0	1.0482	0.7233	0.0105	0.0283	0.557	3.95
19.3	1.0975	0.7408	0.0071	0.0247	0.556	4.02
19.3	1.0975	0.7452	0.0082	0.0247	0.571	4.01

[a] See Table 1. [b] See Table 1; $d = 0.540 \pm 0.022$ mm. [c] See Table 4.

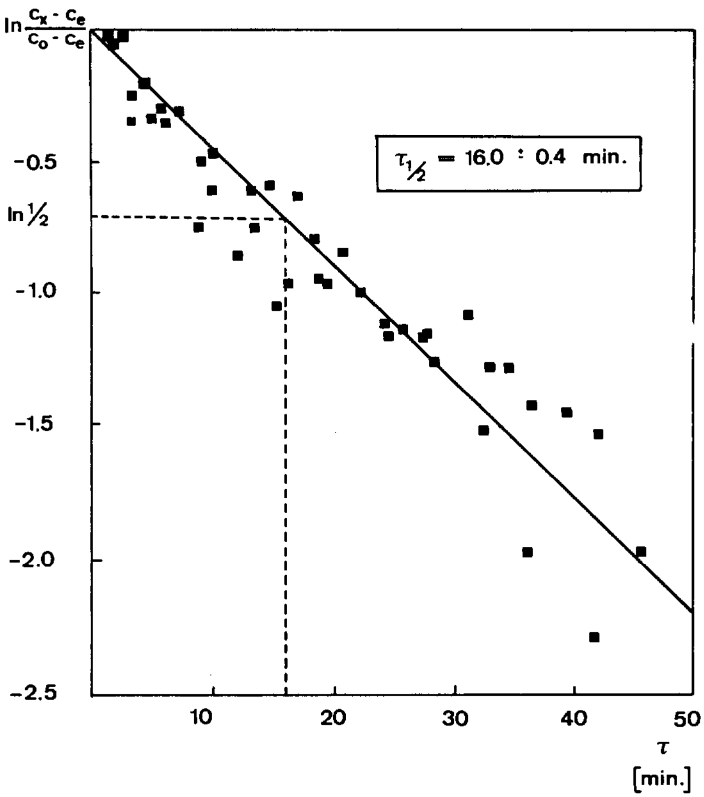

Fig. 7. $Rh_4(CO)_{12} + 4CO \xrightarrow{k_{obs}} 2Rh_2(CO)_8$. Kinetic measurements of the formation reaction of dirhodium octacarbonyl at −22°C and 220 bar carbon monoxide. (c_x = present $Rh_4(CO)_{12}$, c_e = equilibrium concentration of $Rh_4(CO)_{12}$).

eliminate carbon-dioxide, dried over a molecular sieve and stored in aluminium cylinders under pressure.

$Rh_4(CO)_{12}$ was prepared by Chini's method [19] or that of Cattermole et al. [20], and $[Rh(CO)_2Cl]_2$ was obtained from $RhCl_3 \cdot 3H_2O$, as reported by McCleverty and Wilkinson [21].

Hexane ("for UV spectroscopy", Fluka AG, Buchs) was refluxed for several hours over, and distilled immediately before use from, lithium aluminium hydride under carbon monoxide.

Weighed amounts of $Rh_4(CO)_{12}$ were dissolved in 250 to 500 ml hexane to yield initial concentrations of the dodecacarbonyl corresponding to $0.9–1.5 \times 10^{-3}$ mol dm^{-3}. The solution was transferred to a stainless steel autoclave by suction.

Equipment and procedure

The equilibration reactions were carried out in a stainless autoclave of 0.63 dm^3 total capacity, equipped with a magnetically operated, packless stirrer, a calibrated Bourdon type manometer (±1% accuracy) and a platinum resistance thermometer (Pt 100). Samples of the equilibrium mixture were withdrawn and analyzed under the actual conditions (temperature and pressure) by our high-pressure IR equipment, using Noack's type of high-pressure IR cell (cell thickness 0.5 mm) [22] with further development by Dietler [12,23]. The autoclave and the IR cell were cooled by circulating methanol from the cryomat TK 30 (Messgeräte Werk Lauda, West Germany) through the cooling jacket. The temperature of the reaction solution could be kept constant to within ±0.2°C. A further description of the high-pressure equipment used in this work will be given by Dietler et al. [23].

IR spectra were scanned with a Perkin–Elmer Model 325 spectrometer with a spectral slit width of 0.9 cm^{-1} (slit program 4.5). The scanning speed was between 6 and 30 cm^{-1} min^{-1}, depending on the scale expansion. Solvent absorption was compensated for by the use of a commerical variable path length cell.

Determination of the cell thickness as a function of the temperature

Our measurements with Dietler's high pressure IR cell [12,23] were carried out in the temperature range of +30 to −30°C. In this region we observed a relative variation of the cell thickness of ±10%. To obtain quantitatively useful IR spectra, we had to calibrate this effect, which arises from the different temperature dilatation coefficients of the steel and the sodium chloride windows.

The relationship between the cell thickness and the temperature is shown in Fig. 8. This analysis was carried out by IR spectroscopy, using a solution of $Rh_4(CO)_{12}$ in hexane (0.96 mmol dm^{-3}) under 196 bar of nitrogen. The calculations were based on the band at 1886 cm^{-1}, which belongs to the bridging carbonyls of $Rh_4(CO)_{12}$. The deviation of the two points at −24.8 and −28.5°C from the good linear relationship is caused by the lower solubility of the carbonyl at lower temperatures. Using Lambert-Beer's law

$$E = d \times \varepsilon \times c \tag{14}$$

and assuming the independence of the extinction coefficient of the temperature, we obtain

$$\frac{E(T)}{E(0°\text{C})} = \frac{d(T)}{d(0°\text{C})} = 1 + \beta \times T \tag{15}$$

$$\beta = (-4.602 \pm 0.070)\ 10^{-3}\ °\text{C}^{-1}$$

For the correction of a given absorbance at the temperature T to 0°C, we used the following relationship

$$E(0°\text{C}) = \gamma \times E(T) \tag{16}$$

$$\gamma = (1 + \beta \times T)^{-1} \tag{17}$$

The procedure of quantitative analysis

The quantitative analysis of the dodecacarbonyl/octacarbonyl mixture is much more difficult in the rhodium case than for the cobalt compounds. The variation of the cell thickness with temperature did not play a role in the latter case [2] because we scanned all the analytical spectra at the temperature of the instrument, which was 50 to 105°C lower than the temperatures used for the equilibration (90 to 145°C), and thus the reaction was practically stopped during the recording of the spectra. This method evidently could not be used for the rhodium system, where the experimental temperatures were 30 to 80°C lower than the instrument temperature. Hence we were forced to scan the spectra with a cell cooled to the same temperature as the autoclave used for the reaction.

Owing to the impossibility of preparing $Rh_2(CO)_8$ in pure form, the analysis had to be based solely upon the measurement of the intensity of the bridging band of $Rh_4(CO)_{12}$. Hence, in the process of calibration of this work, the following measurements had to be carried out:

(i) the exact determination of the extinction coefficient of the bridging band of $Rh_4(CO)_{12}$ at 1886.9 cm^{-1} (the fulfillment of Beer's law is shown in Fig. 9); the value obtained is $\varepsilon_M = 10{,}760 \pm 80\ cm^{-1}\ mol^{-1}\ dm^3$ *.

(ii) the effect of the high pressure and the lowering of the temperature upon cell thickness was determined by a $Rh_4(CO)_{12}$ solution (in hexane) under nitrogen gas pressure (the temperature effect is shown in Fig. 8).

The accuracy of the data was very satisfactory, and this enabled us to determine precisely the decrease of the $Rh_4(CO)_{12}$ concentration under CO pressure in the temperature range between 20 and −25°C. In fact the spectral changes were observed down to −40°C, but at about −28°C the regularity of the intensity changes ceased, apparently owing to solubility limitations. The solubility of $Rh_4(CO)_{12}$ was obtained in a preliminary measurement (ca. 1 mmol dm^{-3} at −25°C); however, we felt it to be a better strategy not to use such low concentrations which, although they would have allowed us to follow the reaction quantitatively at lower temperatures, would have limited the accuracy of the band intensity measurements.

As a control we also measured the intensities of the two bridging bands of $Rh_2(CO)_8$ at 1862 and 1847 cm^{-1} and calculated their molar extinction coefficients by comparison of the decrease in the known band at 1887 cm^{-1} of $Rh_4(CO)_{12}$ with the increase in the new band at 1847 cm^{-1}. The molar extinction coefficient of the analytical band of $Rh_2(CO)_8$ at 1847 cm^{-1} was calculated from the slope of this line, assuming that the dodeca- and octacarbonyls of rhodium are the only species present in the system.

$$|2\Delta[Rh_4(CO)_{12}]| = |\Delta[Rh_2(CO)_8]| \tag{18}$$

Using Lambert-Beer's law, we obtained:

$$\Delta E = \Delta c \times \varepsilon \times d \tag{19}$$

$$\frac{\Delta E(Rh_2(CO)_8,\ 1847\ cm^{-1})}{\Delta E(Rh_4(CO)_{12}, 1887\ cm^{-1})} = \frac{2\varepsilon(Rh_2(CO)_8,\ 1847\ cm^{-1})}{\varepsilon(Rh_4(CO)_{12}, 1887\ cm^{-1})} \tag{20}$$

$$= 1.119 \pm 0.020$$

$$\varepsilon(Rh_2(CO)_8,\ 1847\ cm^{-1}) = 6020 \pm 110\ cm^{-1}\ mol^{-1}\ dm^3$$

The constancy and the values of the extinction coefficients of the bands belonging to the bridging C–O stretching vibrations of $Rh_2(CO)_8$ (see Table 1) indicate that, in contrast to the isomerism found for $Co_2(CO)_8$ [9], dirhodium octacarbonyl exists (at least in the temperature range studied) only in the bridged form. This result is in agreement with the observations of Hanlan and Ozin [24] in a cryochemical (matrix deposition) experiment: also these authors obtained no evidence for a nonbridged form of $Rh_2(CO)_8$ when a sample prepared by the cocondensation of rhodium metal vapour and carbon monoxide at 15 K was allowed to warm up to about −48°C (at which temperature the sample transformed to $Rh_4(CO)_{12}$ under the high vacuum conditions used in that technique [24]).

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* This value is more accurate than the ε_M we reported previously [17].

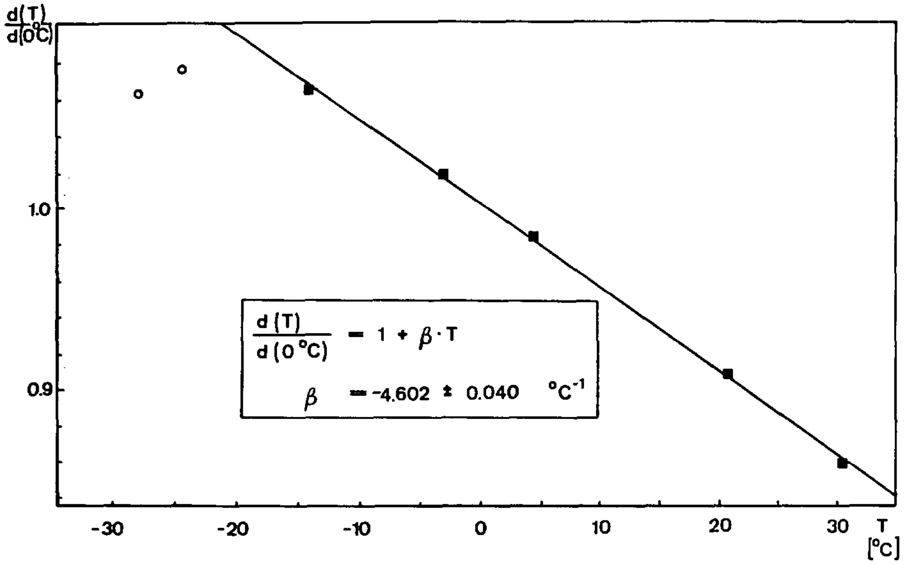

Fig. 8. Relative variation of the cell thickness (d) as function of the temperature (T), as measured by the variation of the $Rh_4(CO)_{12}$ band intensity at 1886.9 cm^{-1}, under constant nitrogen pressure (198 bar). The two points with symbols (o) indicate partial crystallisation of the solute owing to its reduced solubility at these low temperatures.

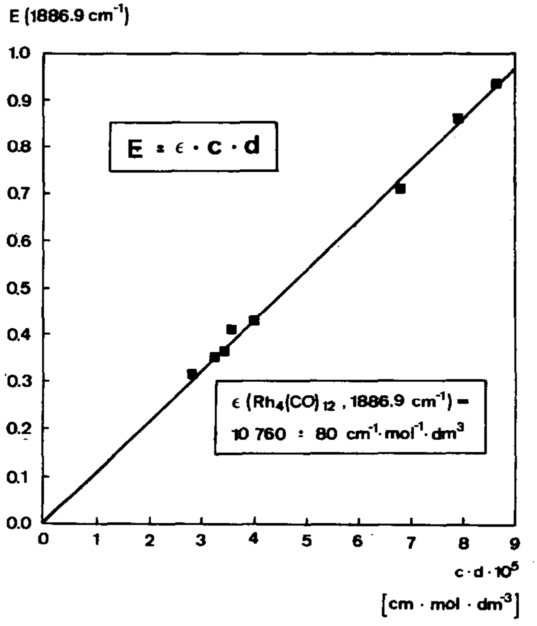

Fig. 9. Determination of the extinction coefficient of the bridging band of $Rh_4(CO)_{12}$ at 1886.9 cm^{-1} using Lambert-Beer's law.

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References

1 R. Ercoli and F. Barbieri-Hermitte, Atti Accad. Naz. Lincei, Cl. Sci. Fis. Mat. Nat. Rend., 16 (1954) 249.

2 G. Bor and U.K. Dietler, J. Organometal. Chem., 191 (1980) 295.

3 (a) P. Pino, F. Piacenti, M. Bianchi in I. Wender, P. Pino (Eds.), Organic Syntheses via Metal Carbonyls, Vol. II. Wiley, New York, 1977; (b) J. Falbe in New Syntheses with Carbon Monoxide, Springer Verlag, Berlin, Heidelberg, New York, 1980.

4 P. Pino, J. Organometal. Chem., 200 (1980) 223.

5 W. Hieber and H. Lagally, Z. Anorg. Allg. Chem., 251 (1943) 96.

6 K. Noack, 8th European Congress on Molecular Spectroscopy, Copenhagen, 1965.

7 (a) B. Heil, G. Bor and L. Markó, unpublished results (1965-66); (b) B. Heil and L. Markó, Chem. Ber., 99 (1966) 1086; (c) B. Heil and L. Markó, ibid., 101 (1968) 2209.

8 P. Chini and S. Martinengo, Inorg. Chim. Acta, 3 (1969) 21 and 299.

9 (a) K. Noack, Spectrochim. Acta, 19 (1963) 1925; (b) G. Bor, ibid., 19 (1963) 1209 and 2065; (c) K. Noack, Helv. Chim. Acta, 47 (1964) 1064 and 1555; (d) G. Bor and K. Noack, J. Organometal. Chem., 64 (1974) 367; (e) G. Bor, U.K. Dietler and K. Noack, J. Chem. Soc. Chem. Commun., (1976) 914; (f) S. Onaka and D.F. Shriver, Inorg. Chem., 15 (1976) 915; (g) R.L. Sweany and T.L. Brown, ibid., 16 (1977) 415.

10 R. Whyman, J. Chem. Soc. Dalton Trans., (1972) 1375.

11 P. Chini and B.T. Heaton, Topics in Curr. Chem., 71 (1977) 1.

12 U.K. Dietler, Dissertation Nr. 5428, ETH-Zürich 1974.

13 G. Bor, G. Sbrignadello and K. Noack, Helv. Chim. Acta, 56 (1975) 815.

14 G. Bor, U.K. Dietler, P. Pino and A. Poë, J. Organometal. Chem., 154 (1978) 301.

15 R. Whyman, personal communication.

16 H. Luther and W. Hiemenz, Chem. Ing. Techn., 29 (1957) 530.

17 F. Spindler, G. Bor, U.K. Dietler and P. Pino, J. Organometal. Chem., 213 (1981) 303.

18 G. Bor, paper presented at the Workshop of the Groups "Clusters and Surfaces" of the Universities Turin, Norwich and Cambridge, 7-8 January 1982, Turin (Italy).

19 P. Chini and S. Martinengo, Inorg. Chim. Acta, 3 (1969) 315.

20 P.E. Cattermole and A.G. Osborne, J. Organometal. Chem., 37 (1972) C17.

21 J.A. McCleverty and G. Wilkinson, Inorg. Synth., 8 (1966) 211.

22 K. Noack, Spectrochim. Acta, 24A (1968) 1917.

23 U.K. Dietler, R. Tannenbaum and G. Bor, manuscript in preparation.

24 L.A. Hanlan and G.A. Ozin, J. Amer. Chem. Soc., 96 (1974) 6324.