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KINETICS AND MECHANISM OF THE REACTION OF TETRACOBALT DODECACARBONYL WITH CARBON MONOXIDE UNDER PRESSURE

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Summary

The kinetics of the reaction of tetracobalt dodecacarbonyl with carbon monoxide to form dicobalt octacarbonyl in n-hexane have been investigated over a wide range of temperature and CO pressure. The reaction is first order in $[Co_4(CO)_{12}]$; the order in [CO] changes between one (at low pressures and high temperatures) and two (at high pressures and low temperatures).

Activation parameters have been estimated and a mechanism involving initial reversible breaking of one Co—Co bond, followed by irreversible breaking of a second, is proposed. The first step involves concerted addition of CO while the second can proceed with or without such addition.

Introduction

In spite of the many studies on a great variety of metal carbonyl derivatives with various ligands much fundamental quantitative kinetic and thermodynamic information is still lacking in the literature regarding the simplest interconversions of the metal carbonyls [1]. This is also the case for the reactions of polynuclear metal carbonyl cluster compounds with carbon monoxide.

A more thorough knowledge of the kinetics and thermodynamics of reactions of type 1 is desirable especially from the point of view of our understanding of

$$M_x(CO)_y + z(CO) \rightarrow nM_{x/n}(CO)_{(z+y)/n} \qquad (1)$$

carbonylation reactions, for which several of these carbonyls act as homogeneous catalysts or catalyst precursors. At temperatures used for catalytic carbonylations, equilibria between carbonyl complexes containing a different number of metal atoms and a different CO/metal ratio can exist, and these may be involved in carbon monoxide activation, which is probably one of the key steps in these catalytic reactions.

As a contribution to this field we report now the results of studies on the kinetics of reaction 2 under carbon monoxide, in n-hexane solution. The reverse

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

of this reaction, i.e. the quantitative thermal conversion of dicobalt octacarbonyl into (tetrameric) "cobalt tricarbonyl" was reported as early as 1910 by Mond, Hirtz and Cowap [2] but the kinetics of that reaction have been studied only recently [3] and only in a limited temperature and pressure range. The reversible character of this reaction was not established until 1948 [4], and no kinetic studies on reaction 2 seem to have been reported so far.

Our results on the determination of the equilibrium constants of reaction 2 in n-hexane solution, as well as kinetic and equilibrium data on similar reactions of iron, ruthenium and rhodium carbonyls will be the subject of subsequent publications.

Experimental

Materials

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

$Co_4(CO)_{12}$ was prepared by heating a toluene solution of $Co_2(CO)_8$ (obtained by the method of Szabó et al. [5]) for several hours at 85—95°C [6], and recrystallized from toluene.

Weighed amounts of $Co_4(CO)_{12}$ were dissolved in approximately 500 ml of hexane to yield ca. $3—4 \times 10^{-3}$ mol dm^{-3} solutions. The solution was transferred into a one-liter stainless steel autoclave by suction, under anaerobic conditions.

Equipment and procedure

The autoclave was equipped with an efficient, magnetically operated packless stirrer ("Dispersimax", Autoclave Engineers, Erie, PA 16512) and heated by means of an oil thermostat which maintained a constant temperature of the reaction solution within ±0.2°C. The total pressure P_{tot} was measured with calibrated Bourdon type manometers of appropriate range and ±1% accuracy. The carbon monoxide partial pressure $p(CO)$ was calculated according to the following equation:

$$p(CO) = P_{tot} - p_0(S) \exp\left\{\frac{V}{RT}(P_{tot} - p_0(S))\right\}$$

where $p_0(S)$ = vapour pressure and V = molar volume, both of the pure solvent at the temperature of the experiment.

This equation accounts for the fact that the solvent vapour pressure depends also on the total pressure, but neglects the interaction between the solvent vapour and carbon monoxide gas and the decrease of the solvent activity in the liquid phase due to dissolved carbon monoxide. The two effects are expected to be small and of opposite sign. Under the above conditions fugacity coefficients of CO are small and have been neglected.

A sampling tube reaching the bottom of the autoclave was connected directly to a flow-through type high pressure infrared cell [7,8]. 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 assembly during this operation by simultaneously feeding carbon monoxide into the autoclave.

On-line sampling was used because it is fast and convenient and because it eliminates the potential error due to the release of a considerable amount of carbon monoxide upon expanding a sample to atmospheric pressure. The spectra were recorded, however, under "semi in situ" conditions (i.e. under working pressure of carbon monoxide but at ambient temperature, ca. 37° C) for two reasons: (i) it is known [9,10] that the spectrum of $Co_2(CO)_8$ changes drastically with temperature, due to the displacement of equilibria between different isomers, making a calibration for quantitative analytical purposes difficult and unreliable; (ii) the technical difficulties of solvent absorption compensation are avoided.

Repeated registration of the spectrum proved that the composition of the sample does not change noticeably during scanning under these conditions.

Spectra were scanned by a Perkin—Elmer Model 325 spectrophotometer. The slit programme 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}. Spectra were recorded between 1890 and 1810 cm^{-1} with 10 × abscissa expansion (i.e. 1 cm^{-1} = 4 mm). Each spectrum was recorded at least twice.

Solvent absorption was compensated for by the use of a commercial variable path cell. With the concentration used, band intensities were optimal for quantitative analysis if the cell thickness was ca. 0.2—0.25 mm.

Quantitative analysis

This was based upon the bridging C—O stretching bands. It was found that the equation reported earlier [11] gave very satisfactory results if the numerical coefficients were slightly modified to account for the higher spectral resolution used in this study, and if the zero-absorption line was accurately adjusted between 1815 and 1800 cm^{-1}.

Equation 3 was used to calculate x, the fraction of cobalt (in a two-component system) present as $Co_4(CO)_{12}$.

$$x = \frac{4[Co_4(CO)_{12}]}{4[Co_4(CO)_{12}] + 2[Co_2(CO)_8]} = \frac{0.409 - 0.232\,Q}{0.336 + Q} \qquad (3)$$

Since we always started from pure $Co_4(CO)_{12}$ solutions, x in this study is obviously identical to the relative concentration of tetracobalt dodecacarbonyl: $[Co_4(CO)_{12}]/[Co_4(CO)_{12}]_0$, and its value is independent of the cell path length and absolute concentration.

In eq. 3 Q is the ratio of the absorbances measured at the two analytical frequencies:

$$Q = \frac{E(1857.7\ cm^{-1})}{E(1867\ cm^{-1})} \qquad (4)$$

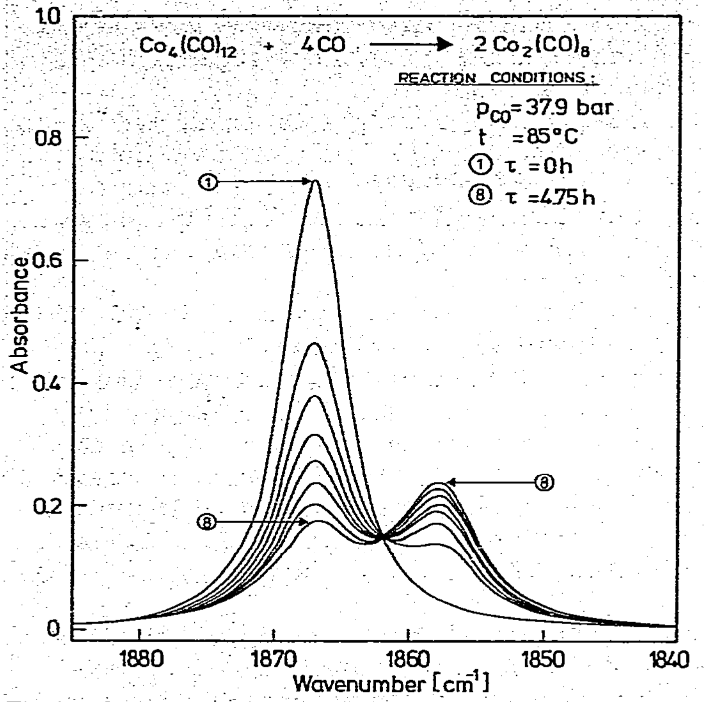

Fig. 1. Infrared absorbance curves in the bridging C—O stretching region taken during a kinetic run.

Here 1857.7 cm^{-1} corresponds to the maximum of the stronger bridging band of $Co_2(CO)_8$, whereas "1867 cm^{-1}" stands for the nearly coinciding maxima of the weaker $Co_2(CO)_8$ band and of the single bridging band of $Co_4(CO)_{12}$. The actual maximum which should be measured, shifts from 1867.3 to 1866.7 cm^{-1} as x decreases from 1 to 0. The spectral curves of one kinetic experiment are shown in Fig. 1.

Results

Operating at constant $p(CO)$ in all cases we obtained plots of $\log([Co_4(CO)_{12}]/[Co_4(CO)_{12}]_0)$ vs. time that were linear for at least 95% conversion proving that the reaction is first order with respect to tetracobalt dodecacarbonyl concentration:

$$\text{rate} = -\frac{d[Co_4(CO)_{12}]}{d\tau} = k_{obs}[Co_4(CO)_{12}] \tag{5}$$

With respect to carbon monoxide pressure the reaction does not obey a simple integer-order rate law. Rather we find an intermediate behaviour between first order (towards higher temperature and low carbon monoxide pressure) and second order (towards low temperature and high CO concentration). This behaviour goes along with a non-linear $\log k_{obs}$ vs. $1/T$ plot: a finding obtained in medium pressure (ca. 40 bar) experiments in a preliminary phase of this study [12].

In order to clarify the origin of this behaviour we investigated the reaction

TABLE 1

KINETIC DATA FOR REACTION $Co_4(CO)_{12} + 4\ CO \rightarrow 2\ Co_2(CO)_8$ AT CONSTANT p(CO)

T (°C)	p(CO) (bar)	$10^{-5}\ k_{obs}$ (s^{-1}) [a]	$\tau_{1/2}$ (h) [b]
37.0	38.3	0.57 ± 0.07	33.8
44.0	39.1	0.91 ± 0.20	21.3
51.0	28.3	0.73 ± 0.03	25.3
	38.0	1.46 ± 0.15	13.2
	77.1	4.53 ± 0.80	4.25
	106.4	8.72 ± 0.28	2.21
65.0	37.7	3.36 ± 0.28	5.73
74.0	4.9	0.36 ± 0.01	53.5
	8.8	0.69 ± 0.01	27.9
	24.4	3.31 ± 0.05	5.81
	39.0	6.88 ± 0.13	2.80
	58.3	13.8 ± 0.4	1.40
	97.3	33.8 ± 0.8	0.57
	116.6	46.7 ± 0.8	0.41
79.4	37.1	9.1 ± 1.0	2.12
85.0	37.9	17.0 ± 0.5	1.13
90.1	36.5	21.2 ± 1.2	0.91
94.5	6.8	4.25 ± 0.15	4.53
	9.8	6.81 ± 0.08	2.83
	50.9	51.6 ± 0.9	0.37
	78.0	92.5 ± 1.2	0.21
96.0	26.7	25.7 ± 1.4	0.75
	36.4	39.8 ± 1.4	0.48
	51.4	55.2 ± 2.5	0.35
	72.6	96.7 ± 5.8	0.20
99.0	38.7	48.6 ± 1.6	0.40
105.6	37.3	81.6 ± 4.6	0.24

[a] k_{obs} calculated according to eq. 5; 95% confidence interval given. [b] Half life time of $Co_4(CO)_{12}$: $\tau_{1/2} = \ln 2/k_{obs}$.

between 35 and 110° C and at constant carbon monoxide pressure between 5 and 120 bar *. The results are compiled in Table 1.

The dependence of the observed rate constants on p(CO) can be accounted for by the following type of empirical equation:

$$k_{obs} = k'_1 p(CO) + k'_2 p^2(CO) \qquad (6)$$

This implies two parallel reaction paths, one of first order and the other of second order in p(CO). Plots of k_{obs}/p(CO) vs. p(CO) proved to be linear to a good degree (cf. Fig. 2) and we can conclude that reactions involving powers of p(CO) lower than one or higher than two do not play a detectable role under the conditions of our experiments.

The k_{obs}/p(CO) vs. p(CO) plots gave us the first estimates for k'_1 and k'_2 at various temperatures. The temperature dependence of these rate constants can

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* 1 bar = 10^5 Pa = 0.98692 atm.

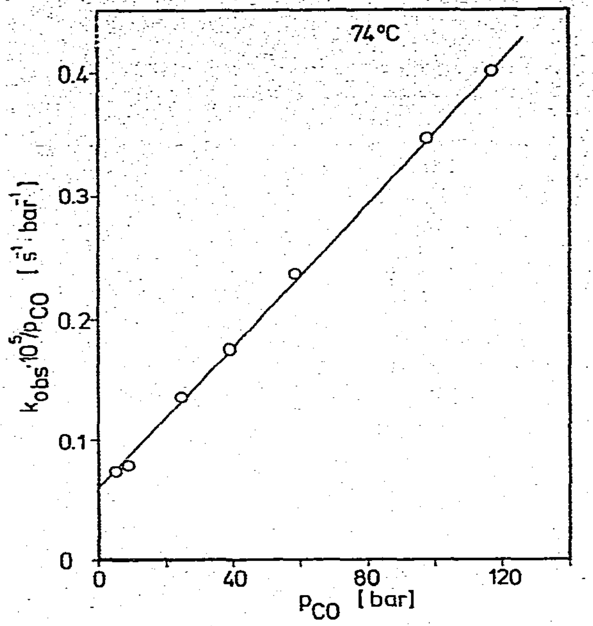

Fig. 2. A $k_{obs}/p(CO)$ vs. $p(CO)$ plot of the experimental results at 74° C.

be expressed as:

$$\ln k_1' = B_{11} - B_{12}/T \quad \text{and} \tag{7}$$

$$\ln k_2' = B_{21} - B_{22}/T \tag{8}$$

The parameters B_{ij} were fitted to the experimental data, in the form of eq. 9 by a non linear least squares procedure *.

$$k_{obs}/p(CO) = \exp\{B_{11} - B_{12}/T\} + \exp\{B_{21} - B_{22}/T\}p(CO) \tag{9}$$

The data were weighed by $1/Y^2$, i.e. the square of the inverse of the response, so that actually the sum of squares of percentage residuals (which are randomly distributed) was minimized.

The following equations were found:

$$\ln k_1' = 26.50(\pm 0.94) - 14170(\pm 470)/T, \quad \text{and}$$

$$\ln k_2' = 0.56(\pm 0.58) - 6220(\pm 210)/T,$$

where k_1' and k_2' are in units of s^{-1} bar^{-1} and s^{-1} bar^{-2} respectively. Figures 3 and 4 show the good agreement (residual root mean square equals 6.3%) between experimental data and calculated curves.

A stepwise linearized least squares procedure based on the two linear eqs. 7 and 8 resulted in very similar coefficients but with a slight bias and larger

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* Non linear least squares curve fitting was effected by the use of a library program of this Department, MNLWOOD, which is a further development of the program GAUSHAUS written originally by D.A. Meeter [29] using Marquardt's Maximum Neighbourhood Method [30]. A complete description of an improved version of D.A. Meeter's program has been published [31].

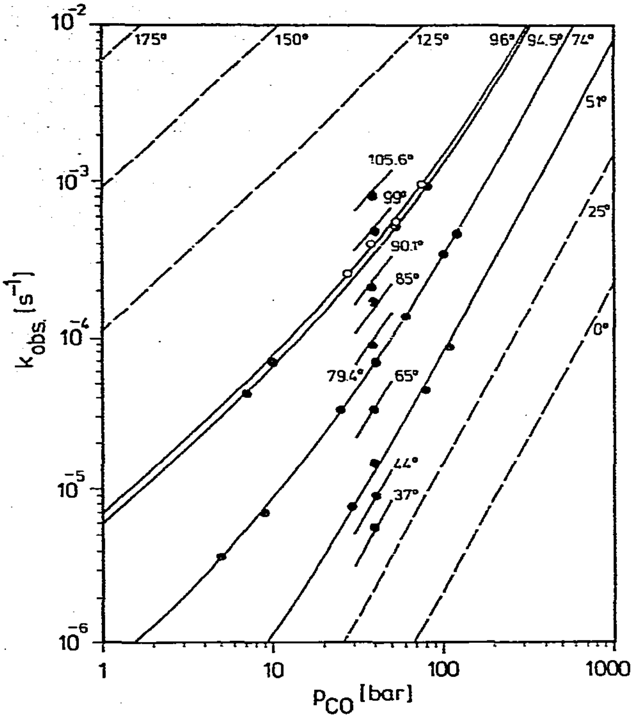

Fig. 3. A log k_{obs} vs. log p(CO) plot of the experimental points (○ at 94.5°C for clarity and ● at 96°C and all other experimental temperatures), and of the curves calculated by the use of eq. 9. Dotted lines are used at temperatures where no experimental values were obtained; these are included to show the trend in the slopes of the isotherms.

standard deviation, as obviously only 19 observations at four different temperatures (51 to 96° C) instead of 27 (from 37 up to 105.6° C) could be used in this way.

From the values B_{ij} ($i,j = 1,2$) the activation parameters $\Delta H_i'^{\ddagger}$ and $\Delta S_i'^{\ddagger}$ (based on the standard state p(CO) = 1 bar) can be calculated according to eq. 10 and 11

$$\Delta H_i'^{\ddagger} = B_{i2}/R - RT \tag{10}$$

$$\Delta S_i'^{\ddagger} = (B_{i1} - \ln \mathrm{e k/h} - \ln T)R \tag{11}$$

where k and h are Boltzmann's and Planck's constants.

In order to obtain values based on the standard state [CO] = 1 mol dm^{-1} we have to rewrite eq. 6 with carbon monoxide concentration instead of pressure:

$$k_{obs} = k_1[\mathrm{CO}] + k_2[\mathrm{CO}]^2 \tag{12}$$

We assume Henry's law is obeyed to a reasonable approximation over the range of pressures used at any given temperature (as proved experimentally at 25° C for iso-octane [8]), i.e. [CO] = αp(CO), and $k_i'/\alpha^i = k_i$ ($i = 1,2$). Consequently the activation parameters related to eq. 12 are given by eq. 13 and 14:

$$\Delta H_i^{\ddagger} = \Delta H_i'^{\ddagger} - i\Delta H_s^0 \tag{13}$$

$$\Delta S_i^{\ddagger} = \Delta S_i'^{\ddagger} - iR \ln \alpha \tag{14}$$

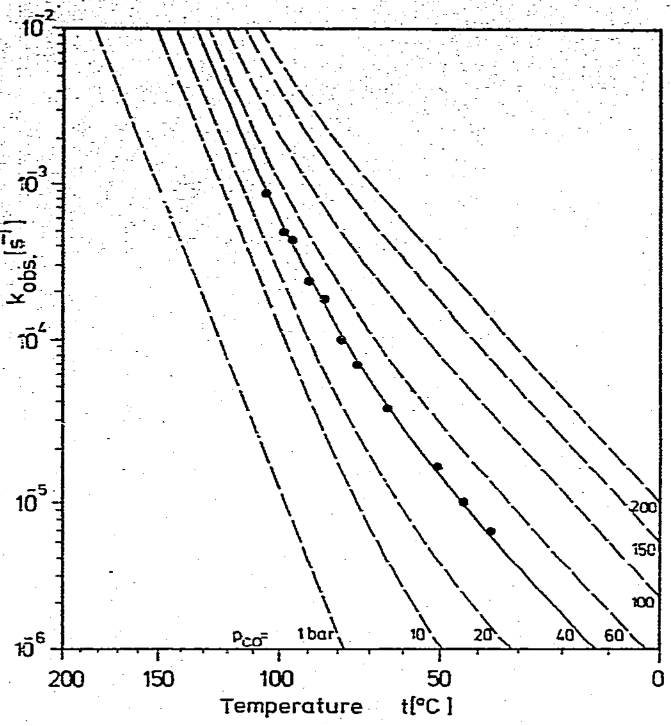

Fig. 4. A log k_{obs} at constant p(CO) vs. $1/T$ plot. The experimental points taken in the pressure interval p(CO) 36—40 bar (see Table 1) were corrected for the common calculated pressure of 40.0 bar according to eq. 6, 7 and 8.

Here ΔH^0_s stands for the enthalpy of solution of carbon monoxide; we judge it to be negligible, in absolute terms and certainly in terms of any chemical interpretation of the activation parameters. Table 2 shows the overall activation parameters calculated by taking $\alpha = 0.012$ mol dm^{-3} bar^{-1}. *

At 97°C $\Delta G^{\ddagger}_1$ equals $\Delta G^{\ddagger}_2$ and therefore k_1 equals k_2. Below this temperature $k_2 > k_1$ while above 97°C $k_1 > k_2$. For the rates of disappearance of $Co_4(CO)_{12}$ over the two paths, this holds true only at a CO concentration of 1 mol dm^{-3} (p(CO) = 83.3 bar with hexane as solvent) because the temperature corresponding to equal rates varies much with p(CO). This fact is clearly demonstrated in Fig. 5, a p(CO)—T diagram of our kinetic results. The curves indicate (p(CO), T) conditions corresponding to equal rate constants (k_{obs}). They are steep in the

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* Values of the solubility of CO in hexane have not been determined over the wide range of temperatures and pressures used in this study. From the available data we estimated the above value according to two approaches: (a) The extrapolation of the solubility data reported for n-heptane [13] and iso-octane [8] yields the value of 0.011 mol dm^{-3} (bar CO)$^{-1}$ for n-hexane. (b) The solubility expressed in molar fractions seems to be approximately constant for paraffinic hydrocarbons, e.g. 1.73×10^{-3} for n-heptane, 1.90×10^{-3} for iso-octane, and 1.81×10^{-3} for a liquid paraffin of mol. wt. 405 [14]. This yields 0.014 mol dm^{-3} bar^{-1} for hexane. The variation of solubility with temperature in different solvents was found to be small [15,16], as shown also by the value of $\Delta H^0_s = 0.9$ kcal mol^{-1} for CO in liquid paraffin [17]. The choice of a value of the solubility is hardly critical since an overestimate even by a factor of 2 merely means that $\Delta S^{\ddagger}_1$ will be 5.9 J K^{-1} mol^{-1} (1.4 cal K^{-1} mol^{-1}) too low, and $\Delta S^{\ddagger}_2$ will be 11.7 J K^{-1} mol^{-1} (2.8 cal K^{-1} mol^{-1}) too low (cf. eq. 14).

TABLE 2

OVERALL ACTIVATION PARAMETERS OF THE TWO REACTION PATHS ($\Delta G_i^{\ddagger}$ at 343 K)

$\Delta G_1^{\ddagger} = 114.2 \pm 6.5$ kJ mol^{-1}	(27.3 ± 1.6 kcal mol^{-1})
$\Delta H_1^{\ddagger} = 115.1 \pm 3.8$ kJ mol^{-1}	(27.5 ± 0.9 kcal mol^{-1})
$\Delta S_1^{\ddagger} = 2.5 \pm 7.9$ J K^{-1} mol^{-1}	(0.6 ± 1.9 cal K^{-1} mol^{-1})
$\Delta G_2^{\ddagger} = 109.4 \pm 3.4$ kJ mol^{-1}	(26.1 ± 0.8 kcal mol^{-1})
$\Delta H_2^{\ddagger} = 49.0 \pm 1.7$ kJ mol^{-1}	(11.7 ± 0.4 kcal mol^{-1})
$\Delta S_2^{\ddagger} = -176.2 \pm 5.0$ J K^{-1} mol^{-1}	(−42.1 ± 1.2 cal K^{-1} mol^{-1})

region where first order rate law in [CO] is dominating: a factor of 10 in p(CO) corresponds to the same factor in k_{obs} at constant temperature. The flatter sections reflect the region where second order behaviour in [CO] is prevailing, since a factor of 10 in p(CO) gives rise to a change by a factor of 10^2 in k_{obs} (at constant temperature). Fractional order in [CO], where the rates over the two paths are of comparable magnitude, is demonstrated by the curved sections and the location of this region of transition depends clearly on T as well as on p(CO).

Two additional pieces of information on the $Co_2(CO)_8/Co_4(CO)_{12}/Co + CO$ system are furnished with Fig. 5 because they impose limits on the observability of the reaction in discussion:

(i) Reaction 2 is actually reversible and at high temperatures and low p(CO) this equilibrium is displaced towards the side of $Co_4(CO)_{12}$. The five parallel

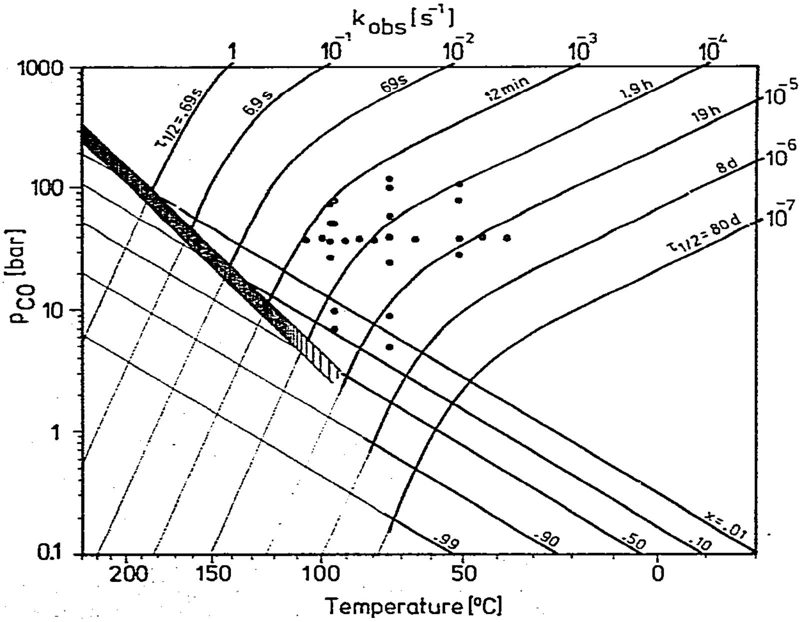


Fig. 5. Curves corresponding to equal k_{obs} values in a log p(CO) vs. T^{-1} diagram. The dots (●) indicate the p–T values of the experimental runs. For description of other features see text. The plot refers to n-hexane solution.

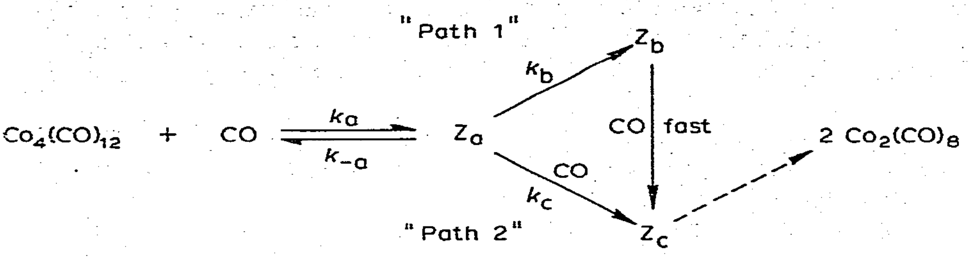
straight lines marked $x = 0.01$ to 0.99 represent $p - T$ conditions corresponding to a given (equal) equilibrium composition [18] (x defined as in eq. 3, total cobalt concentration is 2×10^{-2} mol dm^{-3}).

(ii) The approximate thermal stability limit of the cobalt carbonyls is indicated by the shaded zone (according to ref. 19 and 20; below 110° C, at low p(CO) no data are known, hence this area of the diagram is somewhat uncertain). Decomposition can be quite slow due to its autocatalytic nature [18,19]. Therefore the region of instability has also been included (fine lines).

Discussion

(a) Mechanism

The observed rate equation (eqs. 5, 12) suggests the reaction scheme shown in eq. 15, which is the simplest (among the ones considered) consistent with the experimental data. It corresponds to the rate eqs. 16 and 17 according to the



(15)

two limiting cases where Z_a is conceived of as a steady-state intermediate (formed slowly by reaction with CO and reacting rapidly to form Z_b and Z_c or to re-form $Co_4(CO)_{12}$) or as a product in a rapidly established equilibrium with $Co_4(CO)_{12}$ and CO, and reacting slowly to form Z_b and Z_c *. The two eqs. 16 and 17 differ in the significance of the limiting value of k_{obs} that would

$$-\frac{d[Co_4(CO)_{12}]}{d\tau} = \frac{k_a[CO]\{k_b + k_c[CO]\}k_{-a}}{1 + (k_b + k_c[CO])/k_{-a}}\,[Co_4(CO)_{12}] \tag{16}$$

$$= k_{obs}\,[Co_4(CO)_{12}]$$

$$-\frac{d[Co_4(CO)_{12}]}{d\tau} = \frac{K_a[CO]\{k_b + k_c[CO]\}}{1 + K_a[CO]}\,[Co_4(CO)_{12}] \tag{17}$$

$$= k_{obs}[Co_4(CO)_{12}]$$

$(K_a = k_a/k_{-a})$

be found at sufficiently high values of [CO]. Under these conditions in eq. 16 k_{obs} approaches k_a[CO] i.e. it is the first stage of the reaction that becomes

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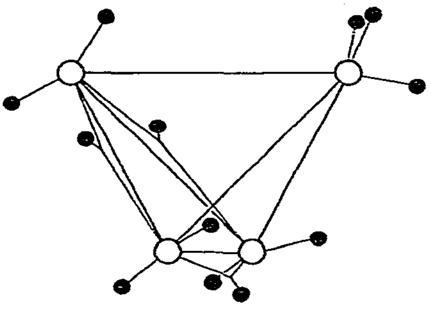
* The principles for the derivation of these kinetic equations are given e.g. by Weissberger [21]. In the case of the mobile prior equilibrium the original kinetic expression $1/2\ d[Co_2(CO)_8]/d\tau = K_a[CO]\{k_b + k_c[CO]\}[Co_4(CO)_{12}]$ was rewritten by the use of a more complete differential form of the cobalt balance, i.e. $4\ d[Co_4(CO)_{12}]/d\tau + 4\ d[Z_a]/d\tau + 4\ d[Z_b]/d\tau + 4\ d[Z_c]/d\tau + 2\ d[Co_2(CO)_8]/d\tau = 0$, where only the changes of $[Z_b]$ and $[Z_c]$ were chosen to be negligible. This yields: $-d[Co_4(CO)_{12}]/d\tau\{1 + K_a[CO]\} = 1/2\ d[Co_2(CO)_8]/d\tau$, and hence eq. 17.

rate determining. In eq. 17 k_{obs} approaches $k_b + k_c[CO]$. Both possibilities involve curvature of plots of $k_{obs}/p(CO)$ against $p(CO)$ at sufficiently high values of $p(CO)$ but eq. 17 implies that this curvature should be accompanied by spectroscopic evidence for the presence of Z_a in finite amounts.

No kinetic or spectroscopic evidence of this kind was found and therefore under all the conditions used $\{k_b + k_c[CO]\}/k_{-a} << 1$ or $K_a[CO] << 1$. In this case both eqs. 16 and 17 then approach our empirical rate equation (eqs. 5, 12) as $k_{obs} = (k_a/k_{-a})k_b[CO] + (k_a/k_{-a})k_c[CO]^2$, and $k_1 = (k_a/k_{-a})k_b$ and $k_2 = (k_a/k_{-a})k_c$ or as $k_{obs} = K_ak_b[CO] + K_ak_c[CO]^2$, and $k_1 = K_ak_b$ and $k_2 = K_ak_c$ respectively. In conclusion no distinction between the two mechanisms is possible on the basis of these kinetic data.

(b) Intermediates

$Co_4(CO)_{12}$ has the structure shown diagrammatically as I [22]. Z_a which according to our scheme should have the formula $Co_4(CO)_{13}$ can most simply be rationalized with the structure II in which each cobalt atom conforms with the 18 electron rule and which derives from I by breaking one cobalt—cobalt bond, making a Co—CO bond, and repositioning one bridging carbonyl group.



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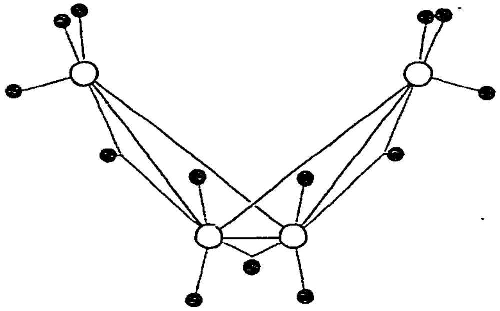


II

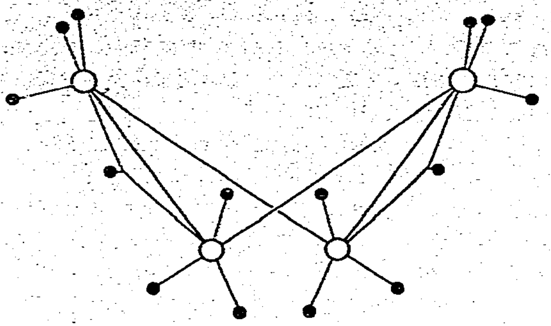
Z_b has, according to our scheme, the same chemical composition as Z_a and should be an unsaturated species.

Z_c has the formula $Co_4(CO)_{14}$. Breaking another metal—metal bond is demanded for any conceivable structure (e.g. III) satisfying the 18 electron rule. This species corresponds to the dimer of the unsaturated complex $Co_2(CO)_7$ postulated by other authors who investigated the reaction $2\ Co_2(CO)_8 \rightarrow Co_4(CO)_{12} + 4\ CO$ [3].

One could assume a disruption of a tetranuclear cluster I or II to yield dinuclear species for Z_b and Z_c within the kinetically limiting two steps (a and b of path 1 and/or a and c of path 2). Such additional breaking of metal—metal bonds should require more energy in $Co_4(CO)_{12}$ or $Co_4(CO)_{13}$ than in $Co_4(CO)_{14}$; therefore this assumption seems less attractive.

(c) Energetics of the reaction

The denominator of eqs. 16 and 17 does not differ significantly from one as shown by the good linearity of the $k_{obs}/[CO]$ plot (cf. Fig. 2). On the basis of our results alone it is therefore not possible to determine the contribution of



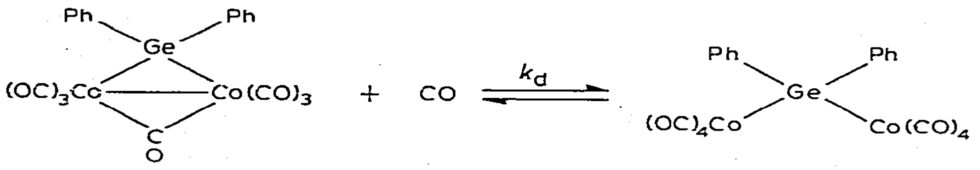
III

the activation parameters of each step in our mechanism to the overall activation parameters $\Delta G_i^\ddagger$, or $\Delta H_i^\ddagger$ and $\Delta S_i^\ddagger$.

Assuming that in the first step equilibrium is reached an estimation of limiting values of the equilibrium constant K_a and hence of $\Delta G_b^\ddagger$ and $\Delta G_c^\ddagger$ (corresponding in this case to the difference between $\Delta G_1^\ddagger$ or $\Delta G_2^\ddagger$ and the standard free energy for the first reaction step, ΔG_a^0) can be made.

By taking the following into consideration, we tried to set at least some limiting values of ΔG_a^0 and ΔH_a^0:

In the reversible step a a metal—metal bond is broken and a metal—CO bond is formed. The difference of the corresponding bond enthalpies [23] yields —10.5 kcal mol^{-1}. This value agrees very well with $\Delta H_a^0 = -11.5$ kcal/mol found [15] for reaction 18, the only well characterized example with features similar to step a *.



(18)

For the overall equilibrium of reaction (2) a standard enthalpy of —30.7 kcal mol^{-1} has been determined [18]; in this reaction four metal—metal bonds are broken and four metal—CO bonds are formed. Hence for step a one fourth of this value is believed to be a reasonable estimate although it is perhaps rather low, since one can argue that breaking the first metal—metal bond together with inserting the first CO group into the stable cluster $Co_4(CO)_{12}$ might yield somewhat less energy than the average. We suggest therefore $\Delta H_a^0 = -8 \pm 4$ kcal mol^{-1} as an estimate.

Limiting values for ΔG_a^0 may be derived from the experimental fact that no $Co_4(CO)_{13}$ (or any intermediate) could be spotted in the IR spectra even at —20°C and 160 bar p(CO) (in sharp contrast to reaction 18, where $Co_2(CO)_8$-($GePh_2$) is formed in significant amounts even at only 1 bar p(CO)). Assuming

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* The conversion of a CO ligand from the bridging into the terminal form and vice versa is known [24,25] to be accompanied by only minor changes in standard enthalpy, and is therefore neglected in this discussion.

that the minimum concentration of $Co_4(CO)_{13}$ to be detected in IR would be 2% or less, one can calculate a value of ΔG^0_a (70°C) $\geq$3 kcal mol^{-1} (to be compared with -4 kcal mol^{-1} found for ΔG^0_d of equilibrium 18 at the same temperature).

A more arbitrary approach has been applied to set an upper limit for ΔG^0_a. On the basis of our assumed ΔH^0_a, a value higher than 8 to 9 kcal mol^{-1} for ΔG^0_a would yield $\Delta S^0_a < -50$ cal mol^{-1} K^{-1} which seems to be very unlikely in view of the entropy value found for reaction 18. Hence we suggest $\Delta G^0_a = +6 \pm 3$ kcal mol^{-1} (corresponding to a 1×10^{-6} to 2×10^{-2} molar fraction of $Co_4(CO)_{13}$.

Table 3 shows the tentative values determined on the basis of these considerations according to the equilibrium hypothesis. Of course the uncertainties, especially the large ones inherent in ΔS^0 and $\Delta S^{\ddagger}$, are correlated.

The fact that reasonable results are obtained by hypothesizing an equilibrium between $Co_4(CO)_{12}$ and the postulated first intermediate $Co_4(CO)_{13}$ does not exclude of course the steady state hypothesis. Indeed the value of $\Delta G^{\ddagger}_a$ (and not the one of ΔG^0_a) relative to $\Delta G^{\ddagger}_b$ and $\Delta G^{\ddagger}_c$ determines if equilibrium conditions in step a are reached. Further comment must be postponed until data for other comparable reactions are determined.

Final remarks

According to our scheme (eq. 15) and the proposed structures for Z_a and Z_c, both steps a and c are bimolecular and involve breaking of a Co—Co bond and addition of a molecule of carbon monoxide. The processes involved in step b and the structure of the corresponding intermediate on the other hand are unknown, though one aspect might be pinpointed on the basis of enthalpy considerations. $\Delta H^{\ddagger}_1$ was found to be more than twice as high as $\Delta H^{\ddagger}_2$. Keeping in mind that $\Delta H^{\ddagger}_c$ should be positive, it follows that $\Delta H^{\ddagger}_b$ is considerably larger than $\Delta H^{\ddagger}_c$ and ΔH^0_a without invoking steady state or equilibrium hypotheses, and it is most probably also larger than $\Delta H^{\ddagger}_a$, since steps a and c both involve

TABLE 3

ESTIMATED THERMODYNAMIC AND ACTIVATION PARAMETERS [a] OF THE DIFFERENT REACTION STEPS ASSUMING A MOBILE EQUILIBRIUM FOR STEP a

ΔG^0_a =	$+25 \pm 13$ kJ mol^{-1}	($+6 \pm 3$ kcal mol^{-1}) [b]
ΔH^0_a =	-33 ± 16 kJ mol^{-1}	(-8 ± 4 kcal mol^{-1}) [b]
ΔS^0_a =	-171 ± 85 J · mol^{-1} K^{-1}	(-40 ± 20 cal mol^{-1} K^{-1})
$\Delta G^{\ddagger}_b$ =	$+89 \pm 19$ kJ mol^{-1}	($+21 \pm 5$ kcal mol^{-1})
$\Delta H^{\ddagger}_b$ =	$+149 \pm 20$ kJ mol^{-1}	($+36 \pm 5$ kcal mol^{-1})
$\Delta S^{\ddagger}_b$ =	$+173 \pm 116$ J · mol^{-1} K^{-1}	($+42 \pm 28$ cal mol^{-1} K^{-1})
$\Delta G^{\ddagger}_c$ =	$+84 \pm 16$ kJ mol^{-1}	($+20 \pm 4$ kcal mol^{-1})
$\Delta H^{\ddagger}_c$ =	$+86 \pm 18$ kJ mol^{-1}	($+20 \pm 4$ kcal mol^{-1})
$\Delta S^{\ddagger}_c$ =	-5 ± 100 J · mol^{-1} K^{-1}	(-1 ± 24 cal mol^{-1} K^{-1})

[a] ΔG values are given for 343 K. [b] Starting estimates discussed in the text; all other values derived from these through the experimental overall kinetic parameters given in Table 2.

similar features. It seems therefore likely that step b should involve the breaking of one metal—metal bond in Z_a and not simply some kind of rearrangement. The parameters compiled in Table 3 clearly do not exclude such a hypothesis either.

Although the aspects regarding the structure of Z_b are mainly speculative, the kinetic patterns of the reaction 2 give the first important insight into the chemical behaviour of $Co_4(CO)_{12}$ towards carbon monoxide. It is straightforward to try to connect these new results with earlier observations on the hydroformylation reaction.

In the stoichiometric hydroformylation [26] in hydrocarbon solution at room temperature only one molecule of carbon monoxide per cobalt atom reacts, the final products being $Co_4(CO)_{12}$ and the aldehyde:

$$CH_2{=}CH_2 + \tfrac{1}{2}\,Co_2(CO)_8 + H_2 \rightarrow CH_3CH_2CHO + \tfrac{1}{4}\,Co_4(CO)_{12} \qquad (19)$$

The fact that when carrying out the reaction under low carbon monoxide pressure (2 bar) [26] no carbon monoxide consumption has been observed, is in keeping with the long time necessary at 25° C and 1 bar CO to transform $Co_4(CO)_{12}$ into $Co_2(CO)_8$ ($\tau_{1/2} \simeq 12$ years). In other words the lack of catalytic activity of $Co_2(CO)_8$ or its derivatives at room temperature and under low p(CO) might be connected with the low rate of the regeneration of $Co_2(CO)_8$ from $Co_4(CO)_{12}$ formed according to reaction 19.

The catalytic hydroformylation of cyclohexene under standard conditions [27] (110° C, $p(CO) = 100$ bar, $p(H_2) = 100$ bar, conc. of $Co_2(CO)_8$ 0.08 mol dm^{-3}, solvent methylcyclohexane) is at least one order of magnitude slower than the formation of $Co_2(CO)_8$ from $Co_4(CO)_{12}$ under the same p(CO), temperature, and type of solvent. This fact indicates that reaction 2 could in principle be responsible for the activation of carbon monoxide in catalytic hydroformylation, as previously proposed [28], although the existence or even the prevalence of other paths involving unstable cobalt carbonyls (e.g. $Co(CO)_3$, II or III) or cobalt carbonyl hydrides cannot be excluded.

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