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KINETICS AND MECHANISM OF THE REACTION BETWEEN DICOBALT OCTACARBONYL AND HYDROGEN

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SUMMARY

The equilibrium and the rates of the reaction between $Co_2(CO)_8$ and H_2 to $HCo(CO)_4$ have been studied in n-heptane at several temperatures. The formation of $HCo(CO)_4$ is first order in both $Co_2(CO)_8$ and H_2 and at low partial pressure of CO is inversely proportional to carbon monoxide concentration. The rate determining step is the reaction of dihydrogen with dicobalt heptacarbonyl, where the latter is formed in a fast pre-equilibrium. Numerical values have been estimated for the pre-equilibrium constant, for the velocity of the rate determining step and for the overall equilibrium constant.

INTRODUCTION

The mechanism of the activation of molecular hydrogen by transition metal complexes is, in a qualitative sense, a rather well known reaction. Practically no quantitative information is available, however, about the energetics of this important process.

The reaction of dicobalt octacarbonyl with dihydrogen was studied in order to gain insight into some details of the splitting of the hydrogen molecule. Due to its considerable significance in connection with the industrial hydroformylation reaction, this reaction has been already repeatedly studied[1,2], the quantitative information available is, however, rather scanty.

EXPERIMENTAL

Experiments were performed in a water- or oil-thermostatted 500 ml magnetic stroke-stirring autoclave filled with oxygen-free n-heptane and solid $Co_2(CO)_8$ in a closed glass bulb. The autoclave was flushed three times and then pressured with the gas to be tested. The reaction was started by breaking the $Co_2(CO)_8$ containing bulb with the magnetic stirrer. The formation of $HCo(CO)_4$ was followed by determining

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TABLE 1

SOLUBILITY OF CO IN n-HEPTANE EXPRESSED IN OSWALD'S ABSORPTION COEFFICIENT (λ)

Temp. (°C)	λ[a]
10	0.346
25	0.386[8]
34	0.408
44	0.434
64	0.486

[a] $\lambda = v/(w \cdot p)$; v=CO volume in ml at 1 atm and 0°; w=weight of heptane in g; p=CO pressure in atm.

the $HCo(CO)_4$ content of the withdrawn liquid samples after various periods of time. The valve and coil for sample-withdrawal were cooled to 0°. Samples were cooled to −80° and stored under CO until titration with 0.02 *N* NaOH to a phenolphthalein end-point[3]. All calculations were made with respect to the volume of gas and liquid in the autoclave, the compressibility of n-heptane[4], vapour pressure and solubility of $HCo(CO)_4$[5,6], and the solubility of H_2[7] and CO[8]. The solubility of CO in n-heptane at various temperatures was measured by the gas saturating method described in the literature[9].

RESULTS

The formation of $HCo(CO)_4$ in n-heptane was found to be first order with respect to both $Co_2(CO)_8$ and H_2. Tables 2 and 3 show the initial rate of formation of $HCo(CO)_4$ at various $Co_2(CO)_8$ and H_2 concentrations.

The dependence on the CO concentration is much more complicated as indicated already by Iwanaga[1], who stated that the rate is inversely proportional to the logarithm of CO partial-pressure under constant pressure of H_2, but that the rate curve at p(CO) 25 atm is different from that at 50 and 100 atm in toluene solution. We have now found, that at appropriately high p(CO) the rate of $HCo(CO)_4$ formation is practically independent of carbon monoxide. At low p(CO), however, the partial-pressure of CO has a strong inhibiting effect on the observed rate. We suggest therefore two competing reaction mechanisms A and B:

A

$$Co_2(CO)_8 \overset{\text{fast } K_D^{(1)}}{\rightleftharpoons} Co_2(CO)_7 + CO \qquad (1)$$

$$Co_2(CO)_7 + H_2 \underset{\text{fast}}{\overset{\text{slow } k_1}{\rightleftharpoons}} H_2Co_2(CO)_7 \qquad (2)$$

$$H_2Co_2(CO)_7 \underset{\text{slow } k_2}{\overset{\text{fast}}{\rightleftharpoons}} HCo(CO)_4 + HCo(CO)_3 \qquad (3)$$

$$HCo(CO)_3 + CO \underset{K_D^{(2)}}{\overset{\text{fast}}{\rightleftharpoons}} HCo(CO)_4 \qquad (4)$$

B

$$Co_2(CO)_8 + H_2 \xrightarrow[k'_1]{\text{slow}} 2\,HCo(CO)_4 \qquad (5)$$

TABLE 2

INITIAL RATE OF $HCo(CO)_4$ FORMATION FROM $Co_2(CO)_8$ AND H_2 IN n-HEPTANE AT 64°

$p_{total} = 160$ atm, $[H_2] = 0.733$ mole/l, $[CO] = 0.661$ mole/l.

$[Co_2(CO)_8] \times 10^2$ (mole/l)	$k_{obs.} \times 10^4$ ($l \cdot mole^{-1} \cdot sec^{-1}$)
0.62	0.29
1.42	0.27
2.78	0.34
2.80	0.32
3.36	0.34
5.50	0.34

TABLE 3

INITIAL RATE OF $HCo(CO)_4$ FORMATION FROM $Co_2(CO)_8$ AND H_2 IN n-HEPTANE AT 44°

$p(H_2) \approx p_{total}$ (atm)	$[H_2]$ (mole/l)	$[Co_2(CO)_8] \times 10^2$ (mole/l)	$k_{obs.} \times 10^4$ ($l \cdot mole^{-1} \cdot sec^{-1}$)
10	0.050	1.93	1.4
19	0.096	2.42	1.92
20	0.101	3.28	2.28
30	0.149	1.52	2.28
55	0.291	1.43	1.98
60	0.321	1.39	2.26
80	0.433	0.88	2.24
97	0.536	0.49	1.83
100	0.554	0.94	2.16
80	0.536	1.08	2.14
100	0.554	1.84	2.0
100	0.554	3.01	2.54
100	0.554	5.24	2.50
110	0.614	1.11	2.37
110	0.614	1.16	1.93
120	0.680	0.89	2.11
137	0.786	1.00	2.40
148	0.853	1.01	2.00
160	0.945	0.91	2.33
180	1.105	0.89	2.56
200	1.218	0.89	2.6

In case A the rate determining step (2) is the reaction of H_2 with $Co_2(CO)_7$, where the latter is formed in a fast pre-equilibrium (1). This would explain the inhibiting effect of carbon monoxide. Mechanism B represents a direct interaction between dicobalt octacarbonyl and hydrogen.

The above schemes lead to the following kinetic relationships:

$$\text{A} \quad d[HCo(CO)_4]/dt = k_1 \cdot K_D^{(1)} \cdot [Co_2(CO)_8] \cdot [H_2] \cdot [CO]^{-1} \tag{6}$$

$$\text{B} \quad d[HCo(CO)_4]/dt = k_1' \cdot [Co_2(CO)_8] \cdot [H_2] \tag{7}$$

The observed rate of $HCo(CO)_4$ formation is thus expressed by

$$(\mathrm{d}[\mathrm{HCo(CO)_4}]/\mathrm{d}t)_{\mathrm{obs.}} = (k_1 \cdot K_\mathrm{D}^{(1)} \cdot [\mathrm{CO}]^{-1} + k_1') \cdot [\mathrm{Co_2(CO)_8}] \cdot [\mathrm{H_2}] \tag{8}$$

and

$$k_{\mathrm{obs.}} = k_1 \cdot K_\mathrm{D}^{(1)} \cdot [\mathrm{CO}]^{-1} + k_1' \tag{9}$$

k_1' is equal to $k_{\mathrm{obs.}}$ if $p(\mathrm{CO}) \rightarrow \infty$ and was derived graphically from the experimental data. By abstracting k_1' from $k_{\mathrm{obs.}}$ the CO dependent part of the observed rate constant could be separated:

$$k_{\mathrm{obs.}} - k_1' = k_1 \cdot K_\mathrm{D}^{(1)} \cdot [\mathrm{CO}]^{-1} \tag{10}$$

and

$$(k_{\mathrm{obs.}} - k_1') \cdot [\mathrm{CO}] = k_1 \cdot K_\mathrm{D}^{(1)} = \text{const.} \tag{11}$$

The validity of this relationship is illustrated by the experimental results in Table 4.

In experiments initiated in the absence of CO *e.g.* in an atmosphere of H_2, a certain CO concentration must almost instantly appear due to the fast pre-equilibrium. From the initial rate obtained in these experiments and those measured at known $p(\mathrm{CO})$, the CO concentration furnished by the pre-equilibrium can be calculated. This makes the estimation of the pre-equilibrium constant possible. Table 5 lists these constants derived from measurements at various temperatures.

The data were used to calculate the thermodynamic and activation parameters of the reactions (1), (2) and (5).

$$\begin{array}{lll} \text{reaction (1)} & \Delta H = 21\ \text{kcal/mole} \\ & \Delta S = 48\ \text{e.u.} \\[1ex] \text{reaction (2)} & \Delta H^{\ddagger} = 7\ \text{kcal/mole} \\ & \Delta S^{\ddagger} = -49\ \text{e.u.} \\[1ex] \text{reaction (5)} & \Delta H^{\ddagger} = 25\ \text{kcal/mole} \\ & \Delta S^{\ddagger} = -6\ \text{e.u.} \end{array}$$

TABLE 4

INITIAL RATE OF $HCo(CO)_4$ FORMATION FROM $Co_2(CO)_8$ AND H_2 IN n-HEPTANE AT 64° AT VARIOUS [CO]

p_{total} (atm)	[CO] (mole/l)	$[H_2]$ (mole/l)	$[Co_2(CO)_8] \times 10^2$ (mole/l)	$k_{\mathrm{obs.}} \times 10^4$ ($\mathrm{l \cdot mole^{-1} \cdot sec^{-1}}$)	$(k_{\mathrm{obs.}} - k_1')^a \times 10^4$ ($\mathrm{l \cdot mole^{-1} \cdot sec^{-1}}$)	$(k_{\mathrm{obs.}} - k_1') \cdot [\mathrm{CO}] \times 10^6$ ($\mathrm{sec^{-1}}$)
98	0.025	0.574	2.30	1.74	1.48	3.7
100	0.051	0.580	2.84	1.01	0.75	3.8
160	0.084	0.989	3.13	0.64	0.38	3.2
120	0.109	0.687	1.65	0.55	0.29	3.2
20	0.188	0.032	3.22	0.45	0.19	3.5
60	0.238	0.245	2.70	0.44	0.18	4.2
160	0.433	0.831	1.65	0.32	0.06	2.6
160	0.661	0.733	2.80	0.32	0.06	3.9
160	1.037	0.569	2.76	0.29	0.03	3.1
160	1.465	0.325	3.35	0.28	0.02	2.9
160	0.433	0.831	2.53	0.33	0.07	3.0
80	0.210	0.377	2.50	0.39	0.13	2.3
40	0.104	0.183	2.46	0.57	0.31	3.2
20	0.051	0.091	2.50	0.89	0.63	3.3

[a] Value of $k_1' = 0.26 \times 10^{-4}\ \mathrm{l \cdot mole^{-1} \cdot sec^{-1}}$ at 64°.

TABLE 5

EQUILIBRIUM CONSTANT $K_D^{(1)}$ OF REACTION (1) AND REACTION VELOCITY CONSTANTS k_1 OF REACTION (2) AND k_1' OF REACTION (5) AT DIFFERENT TEMPERATURES

Temp. (°C)	$k_1 \cdot K_D^{(1)} \times 10^8$ (sec^{-1})	$K_D^{(1)} \times 10^4$ (mole/l)	$k_1 \times 10^4$ ($l \cdot mole^{-1} \cdot sec^{-1}$)	$k_1' \times 10^6$ ($l \cdot mole^{-1} \cdot sec^{-1}$)
34	4.4	0.39	11.4	–
44	20.7	1.23	16.8	2.3
54	79.8	3.25	24.5	8.0
64	314	10.3	30.5	26.0

To obtain more information about the rupture of the H–H bond, experiments were performed with D_2 at 34° and 20 atm total pressure of D_2. The ratio of the observed initial rate $k(H_2)/k(D_2)$ varied between 2.0–2.6.

The equilibrium of the overall reaction (12) was determined between 34° and 155°.

$$Co_2(CO)_8 + H_2 \overset{K}{\rightleftarrows} 2\ HCo(CO)_4 \qquad (12)$$

Time required to reach equilibrium varied with the experimental conditions from 2 to 80 h. Calculation of K was based on the measured concentration of $HCo(CO)_4$ in equilibrium and on the initial concentrations of $Co_2(CO)_8$ and H_2. The plot of log K against the reciprocal of absolute temperature can be seen in Fig. 1. The thermodynamic parameters for equilibrium (12) are:

$$\Delta H = 3.2 \text{ kcal/mole and } \Delta S = 4.4 \text{ e.u.}$$

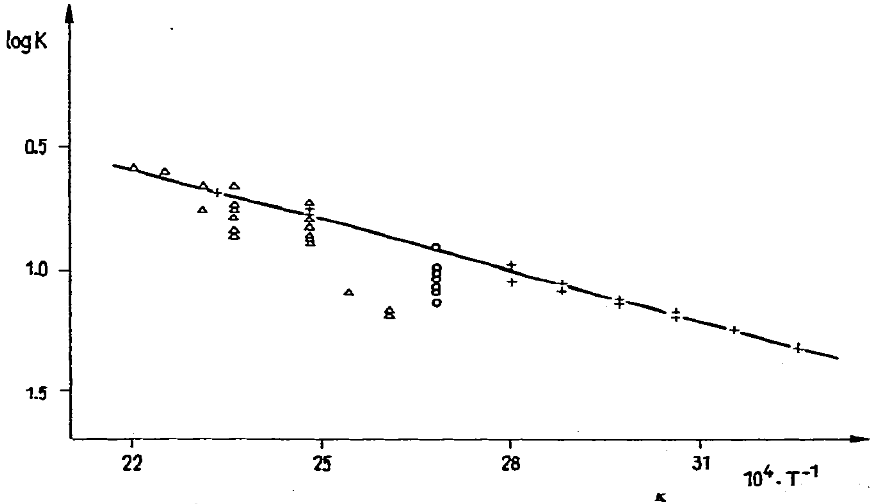


Fig. 1. log $K - T^{-1}$ for the equilibrium reaction $Co_2(CO)_8 + H_2 \overset{K}{\rightleftarrows} 2\ HCo(CO)_4$. △ measured in toluene[6]; ○ measured in toluene[1]; + our results measured in n-heptane.

In equilibrium

$$-d[HCo(CO)_4]/dt = +d[HCo(CO)_4]/dt \tag{13}$$

expressed with the kinetic equations valid for the low p(CO) region

$$k_2 \cdot K_D^{(2)} \cdot [HCo(CO)_4]^2 \cdot [CO]^{-1} = 2 \cdot k_1 \cdot K_D^{(1)} \cdot [Co_2(CO)_8] \cdot [CO]^{-1} \tag{14}$$

and

$$K = \frac{[HCo(CO)_4]^2}{[Co_2(CO)_8] \cdot [H_2]} = \frac{2 \cdot k_1 \cdot K_D^{(1)}}{k_2 \cdot K_D^{(2)}} \tag{15}$$

Table 6 shows numerical values of the equilibrium constant K determined by the above static method compared with those derived from the kinetic data of the forward and reverse[5] reaction.

TABLE 6

EQUILIBRIUM CONSTANTS FOR REACTION (12) IN n-HEPTANE DERIVED BY THE STATIC AND KINETIC METHODS

Temp. (°C)	$K = \frac{[HCo(CO)_4]^2}{[Co_2(CO)_8] \cdot [H_2]} \times 10^2$	$K = \frac{2 \cdot k_1 \cdot K_D^{(1)}}{k_2 \cdot K_D^{(2)}} \times 10^2$
34	4.6	4.50
44	5.5	5.74
54	6.5	6.49
64	7.6	7.33

[a] Values of $k_2 \cdot K_D^{(2)}$ used[5] are extrapolated from 25°.

DISCUSSION

The rate of ^{14}CO exchange for $Co_2(CO)_8$[10] supports our assumption that the pre-equilibrium (1) is a very fast reaction. $Co_2(CO)_8$ undergoes CO exchange by a dissociative process in which the rate determining step is the loss of CO. The reported ^{14}CO exchange rate is much greater than the reaction velocity observed with H_2. The recombination reaction of the coordinatively unsaturated $Co_2(CO)_7$ and CO must also be very fast, since equilibrium (1) lies far on the side of $Co_2(CO)_8$.

The observed kinetic isotope effect indicates that the hydrogen–hydrogen bond is markedly affected, perhaps completely broken, in the rate determining step.

As estimated from pre-equilibrium (1) 21 kcal are needed for $Co_2(CO)_8$ to abstract one molecule of CO. For $HCo(CO)_4$ however, a value of 13 kcal was reported[5] for the same process. The lower energy requirement in the latter molecule is probably due to the hydrogen atom present.

The free energy changes during the whole reaction are illustrated in Fig. 2.

The data allow some conclusions about the energetics of the Co–H bond formation. In the reaction of $Co_2(CO)_8$ and H_2 the Co–Co and the H–H bonds are split and two new Co–H bonds are formed. The reaction is slightly endothermic: $\Delta H = 3.2$ kcal/mole. The enthalpies of dissociation for $Co_2(CO)_8$[11] and H_2[12] are known:

$$Co_2(CO)_8 \rightleftarrows 2\,{}^{\bullet}Co(CO)_4 \quad \Delta H = 14.5 \pm 2 \text{ kcal/mole}$$

$$H_2 \rightleftarrows 2\,{}^{\bullet}H \quad \Delta H = 104.2 \text{ kcal/mole}$$

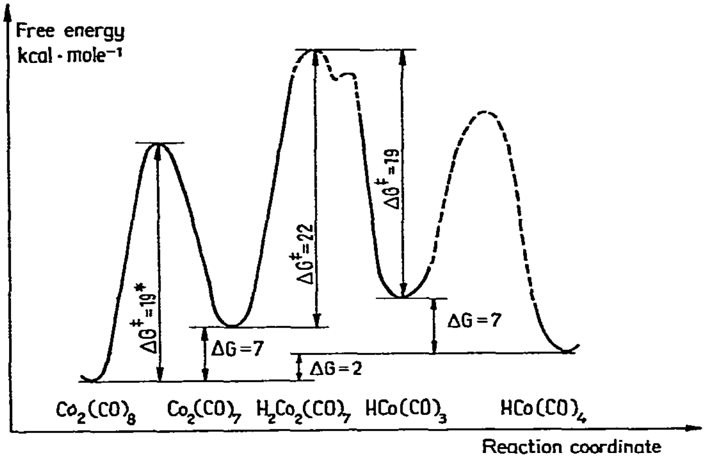
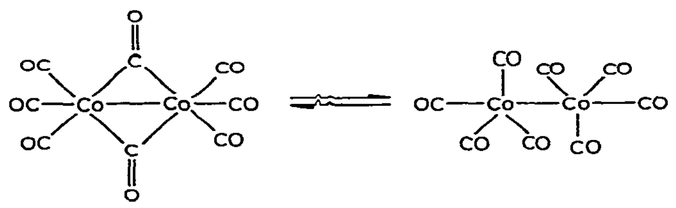


Fig. 2. Energy pathway for the reaction $Co_2(CO)_8 + H_2 \rightleftharpoons 2\ HCo(CO)_4$. The $\Delta G^{\ddagger}$ [19 kcal·mole^{-1} for $Co_2(CO)_8$] were calculated based on the work of Basolo *et al.*[10].

If we summarize the known enthalpy changes, we obtain about 58 kcal which is furnished by the formation of one molecule $HCo(CO)_4$. This energy is the sum of the Co–H bonding energy and the energy set free by rearranging the CO groups in $HCo(CO)_4$ as compared to their positions in the $\cdot Co(CO)_4$ radical. Such rearrangements do not consume much energy as can be seen from the enthalpy difference between the two forms of $Co_2(CO)_8$ as reported by Noack[13]:



$\Delta H = 1.3$ kcal/mole

The 58 kcal/mole can be therefore roughly considered as the energy of the Co–H bond in $HCo(CO)_4$.

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