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KINETICS OF TETRACOBALT DODECACARBONYL FORMATION FROM DICOBALT OCTACARBONYL IN HEPTANE

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Summary

The decomposition of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ in heptane can be described by the kinetic equation:

$$\frac{d[Co_4(CO)_{12}]}{dt} = k_{obs} \cdot \frac{[Co_2(CO)_8]^2}{[CO]^2}$$

Dicobalt heptacarbonyl formed in a fast pre-equilibrium:

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

is a possible intermediate of the reaction. The values for the equilibrium constant K_D^1 calculated from the kinetics of $Co_2(CO)_8$ decomposition are in good agreement with results from independent measurements.

Introduction

Complex formation, hydrogenation, hydroformylation and isomerization take place when olefins, diolefins or acetylenes react with synthesis gas in the presence of cobalt carbonyls. Most of these reactions are inhibited by carbon monoxide [1], a fact which provides strong support for the assumptions that coordinatively unsaturated cobalt carbonyls act as reactive intermediates in the above reactions.

From the study of the reaction between dicobalt octacarbonyl and dihydrogen in heptane:

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2\,HCo(CO)_4$$

quantitative data in form of equilibrium constants are known for the possible intermediates $Co_2(CO)_7$ [2] and $HCo(CO)_3$ [3]. $Co_2(CO)_7$ and $Co_2(CO)_6$ are possibly intermediates in the case of $Co_4(CO)_{12}$ formation from $Co_2(CO)_8$ in toluene [4], but further investigation has shown that the kinetics of this reaction are strongly dependent on the solvent used; the order of carbon monoxide changes from —4 in toluene to —3 in heptene, and to —2 in heptane.

We report now on the kinetics of $Co_4(CO)_{12}$ formation from $Co_2(CO)_8$ in heptane as solvent. The data allow an independent calculation of the equilibrium constant for the dissociation of $Co_2(CO)_8$ to give the coordinatively unsaturated $Co_2(CO)_7$.

Experimental

Experiments were carried out in a thermostatted flask equipped with a gas-tight stirrer and connected to a thermostatted gas burette. First the reaction flask was repeatedly evacuated and purged with argon or carbon monoxide or with a mixture of these gases. In a continous gas flow a known amount of solid dicobalt octacarbonyl in a small PTFE-container was placed in a moveable side arm of the reactor flask. The dioxygen- and water-free solvent was saturated with the appropriate gas and added by a syringe through a silicon rubber cap. After vapour-liquid equilibrium has been attained the reaction was started by turning the side arm. The fine crystalline dicobalt octacarbonyl in the PTFE container fell into the solvent and dissolved within five seconds. The reaction was followed by recording the volume of carbon monoxide evolved.

All experiments were carried out at atmospheric pressure.

Results and discussion

The formation of $Co_4(CO)_{12}$ from $Co_2(CO)_8$ in heptane in the presence of carbon monoxide was found to be of second order with respect to $Co_2(CO)_8$ and of an order of —2 with respect to carbon monoxide:

$$r = \frac{d[Co_4(CO)_{12}]}{dt} = k_{obs} \cdot \frac{[Co_2(CO)_8]^2}{[CO]^2} \qquad (1)$$

where k_{obs} = the observed rate constant ($mole \cdot l^{-1} \cdot sec^{-1}$) and all concentrations respond to the liquid phase ($mole \cdot l^{-1}$).

Table 1 and 2 show the initial rates of $Co_4(CO)_{12}$ formation at several

TABLE 1

INITIAL RATES OF $Co_4(CO)_{12}$ FORMATION AT VARIOUS $Co_2(CO)_8$ CONCENTRATIONS IN HEPTANE UNDER CARBON MONOXIDE ATMOSPHERE

(Total pressure: 1 atm.)

Temp. (°C)	$[CO]_{liq} \times 10^2$ ($mole \cdot l^{-1}$)	$[Co_2(CO)_8] \times 10^2$ ($mole \cdot l^{-1}$)	$r \times 10^7$ ($mole \cdot l^{-1} \cdot sec^{-1}$)	$r \times 10^4/[Co_2(CO)_8]^2$ ($l \cdot mole^{-1} \cdot sec^{-1}$)
65	0.904	0.885	0.297	3.8
	0.902	1.83	1.34	4.0
	0.908	4.07	6.72	4.0
75	0.734	2.16	26.4	56
	0.731	2.53	33.0	52
	0.734	2.83	42.3	53
	0.739	4.33	99.5	53
	0.739	5.44	170	57

TABLE 2

INITIAL RATES OF $Co_4(CO)_{12}$ FORMATION AND THE OBSERVED RATE CONSTANTS ($k_{obs} = r_{CO} \times [CO]^2_{liq}/[Co_2(CO)_8]^2$) AT SEVERAL TEMPERATURES UNDER VARIOUS PARTIAL PRESSURES OF CARBON MONOXIDE IN HEPTANE

(Total pressure: 1 atm.)

Temp. (°C)	$[Co_2(CO)_8] \times 10^2$ (mole·l^{-1})	$[CO]_{liq} \times 10^2$ (mole·l^{-1})	$r \times 10^8$ (mole·l^{-1}·sec^{-1})	$k_{obs} \times 10^8$ (l·mole^{-1}·sec^{-1})
45	2,49	0.114	72	0.15
55	1.96	0.109	258	0.80
	1.91	0.203	62	0.70
	1.87	0.203	63	0.75
	1.94	0.516	10.0	0.70
	2.23	0.640	8.5	0.70
65	2.01	0.180	384	3.1
	1.84	0.453	53	3.2
	1.83	0.902	13.5	3.25
75	2,16	0.734	264	30

temperatures and at various dicobalt octacarbonyl and CO concentrations. The temperature dependence of the observed rate constant is shown by eqn. (2):

$$\lg k_{obs} = [-7100/T] + 13.5 \qquad (2)$$

The negative second order dependence on carbon monoxide suggests that two molecules of carbon monoxide are involved in fast pre-equilibria. Among the many possibilities for these pre-equilibria, the two most simple are:

$$Co_2(CO)_8 \overset{K_D^1}{\rightleftharpoons} Co_2(CO)_7 + CO \qquad (3)$$

$$Co_2(CO)_7 \rightleftharpoons Co_2(CO)_6 + CO \qquad (4)$$

Since the concentration of $Co_2(CO)_6$ will certainly be much smaller than that of $Co_2(CO)_7$, it is the first equilibrium (3) which will mainly be responsible for the initial carbon monoxide concentration in experiments started under argon. This initial carbon monoxide concentration $[CO]_{Ar}$ can be estimated from the initial rates according to:

$$\frac{r_{CO}}{r_{Ar}} = \frac{[CO]^2_{Ar} \cdot [Co_2(CO)_8]^2_{CO}}{[CO]^2_{CO} \cdot [Co_2(CO)_8]^2_{Ar}} \qquad (5)$$

$$[CO]_{Ar} = \left[\frac{r_{CO}/[Co_2(CO)_8]^2_{CO} \cdot [CO]^{-2}_{CO}}{r_{Ar}/[Co_2(CO)_8]^2_{Ar}}\right]^{1/2} = \left[\frac{k_{obs}}{r_{Ar}/[Co_2(CO)_8]^2_{Ar}}\right]^{1/2} \qquad (6)$$

where the index Ar and CO refer to values used or obtained in experiments started under argon or a known partial pressure of carbon monoxide, respectively. The values of $r_{Ar}/[Co_2(CO)_8]^2_{Ar}$ obtained at constant gas/liquid volume ratios can be seen in Table 3. Using these and the values of k_{obs} obtained earlier, K_D^1 may be calculated by eqns. (6) and (3) (see Table 4).

TABLE 3

VALUES OF $r_{Ar}/[Co_2(CO)_8]^2_{Ar}$ CALCULATED FROM THE INITIAL RATES OF $Co_4(CO)_{12}$ FORMATION IN HEPTANE

(Total pressure: 1 atm, volume ratio of the gas and liquid phase: $V_{gas}/V_{liq} = 20$.)

Temp. (°C)	$r_{Ar}/[Co_2(CO)_8]^2_{Ar}$ (l·mole^{-1}·sec^{-1})			
$[Co_2(CO)_8]_{Ar}$ (mole·l^{-1}):	0.005	0.01	0.02	0.025
25	0.115	0.047	0.020	0.015
35	0.27	0.105	0.042	0.031
45	0.55	0.215	0.083	0.061
55		0.415	0.158	0.115

TABLE 4

EQUILIBRIUM CONSTANT K_D^1 IN HEPTANE AT VARIOUS TEMPERATURES

Temp. (°C)	$K_D^1 \times 10^4$ (mole·l^{-1})			
$[Co_2(CO)_8]$ (mole·l^{-1}):	0.005	0.01	0.02	0.025
25	0.09	0.10	0.11	0.11
35	0.26	0.29	0.33	0.34
45	0.98	0.91	0.98	1.01
55		4.1	3.4	3.3

The temperature dependence of this dissociation constant is described by the equation:

$$\lg K_D^1 = -4840/T + 11.25 \qquad (7)$$

This may be compared with eqn. (8), which shows the temperature dependence for the same constant as estimated earlier [2] from the kinetic data of the reaction between $Co_2(CO)_8$ and H_2:

$$\lg K_D^1 = -4680/T + 10.8 \qquad (8)$$

The reasonable agreement between eqn. (7) and (8) provides further indirect evidence for the existence of $Co_2(CO)_7$. To give some idea of the expected concentration of this unsaturated species under the usual conditions of experimental work with $Co_2(CO)_8$ it may be mentioned that the values of K_D^1 suggest the presence of about 0.1% of $Co_2(CO)_7$ based on $Co_2(CO)_8$ at 1 atm p_{CO} and 25°.

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