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KINETICS AND MECHANISM OF THE DECOMPOSITION OF COBALT TETRACARBONYL HYDRIDE TO DICOBALT OCTACARBONYL AND HYDROGEN

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SUMMARY

The decomposition of cobalt tetracarbonyl hydride to dicobalt octacarbonyl and hydrogen in n-heptane follows the kinetic equation

$$-\frac{d[HCo(CO)_4]}{dt}=\frac{k_2\cdot K}{p_{CO}}\cdot[HCo(CO)_4]^2$$

The rate determining step is a reaction between $HCo(CO)_3$ and $HCo(CO)_4$, which does not involve the cobalt–hydrogen bonds. The concentration of $HCo(CO)_3$ in equilibrium with $HCo(CO)_4$ can be calculated.

INTRODUCTION

The decomposition of cobalt tetracarbonyl hydride to dicobalt octacarbonyl and hydrogen

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

is a rather important reaction, since both complexes can be regarded as the catalysts of the industrial hydroformylation (or oxo) reaction. This decomposition has already been studied in some detail in the gas phase[1-3], but the results were badly reproducible and therefore difficult to interpret. No efforts have been made to investigate the reaction in solution, although hydroformylation is carried out in the liquid phase and it is thus the decomposition of dissolved $HCo(CO)_4$, which is principally of interest.

The most generally accepted mechanism of hydroformylation[4] assigns an important role to the hypothetical cobalt tricarbonyl hydride, formed from cobalt tetracarbonyl hydride by the loss of one carbon monoxide ligand:

$$HCo(CO)_4 \rightleftarrows HCo(CO)_3+CO$$

No evidence has been previously offered, however, for the existence of this coordinatively unsaturated, very reactive species.

Reported in this paper are our studies on the kinetics of decomposition of $HCo(CO)_4$ in hydrocarbon solvents. The results give information about the mechanism of this reaction, and allow the determination of the concentration of $HCo(CO)_3$ in equilibrium with dissolved $HCo(CO)_4$.

EXPERIMENTAL

n-Heptane solutions of $HCo(CO)_4$[5,6] and $DCo(CO)_4$[7,8] were prepared as described in the literature, and stored at −80°.

Experiments were carried out in a thermostatted flask equipped with a gas-tight stirrer and connected to a thermostatted gas burette. The reaction flask was first repeatedly evacuated and purged with hydrogen, nitrogen, or carbon monoxide or a mixture of these gases, then n-heptane was added with a syringe through a silicone rubber cap. When vapour-liquid equilibrium was reached, the reaction was started by introducing the heptane solution of $HCo(CO)_4$ or $DCo(CO)_4$ in the same way. The decomposition was followed gasometrically by the volume of hydrogen evolved.

Allowance was made for the concentration of $HCo(CO)_4$ in the gas phase. This was accomplished by taking a sample from the gas phase, absorbing its $HCo(CO)_4$ content in acetone and determining the cobalt concentration in this solution. The results of these determinations are shown in Table 1.

TABLE 1

MOLE PER CENT $HCo(CO)_4$ IN THE GAS PHASE ABOVE A HEPTANE SOLUTION CONTAINING 1 mmole $HCo(CO)_4$/ml

Temp. (°C)	Mole per cent
10	1.84
15	2.63
20	3.70
25	5.00

The purity of $DCo(CO)_4$ was established by determining by mass spectrometry the D_2 content of the gas evolved during decomposition. It was found to be not less than 92%.

RESULTS

The decomposition was found to be second order with respect to the $HCo(CO)_4$ taken. Experiments in gas mixtures with different concentrations of carbon monoxide showed that it inhibited the reaction in proportion to its partial pressure.

These observations suggest the following mechanism:

$$HCo(CO)_4 \overset{K}{\rightleftharpoons} HCo(CO)_3 + CO \tag{1}$$

$$HCo(CO)_3 + HCo(CO)_4 \xrightarrow{k_2} H_2Co_2(CO)_7 \tag{2}$$

$$H_2Co_2(CO)_7 \xrightarrow{\text{fast}} H_2 + Co_2(CO)_7 \tag{3}$$

$$Co_2(CO)_7 + CO \xrightarrow{\text{fast}} Co_2(CO)_8 \tag{4}$$

The above scheme leads to the kinetic relationship (5).

$$-\frac{d[\mathrm{HCo(CO)_4}]}{dt}=\frac{k_2\cdot K}{p_{\mathrm{CO}}}\cdot[\mathrm{HCo(CO)_4}]^2 \tag{5}$$

The experimental results furnish the overall velocity constant k_{H} given by eqn. (6).

$$k_{\mathrm{H}}=\frac{k_2K}{p_{\mathrm{CO}}} \tag{6}$$

To evaluate the product k_2K, experiments were conducted at definite carbon monoxide partial pressures. The results are shown in Table 2.

TABLE 2

RATE OF DECOMPOSITION OF $\mathrm{HCo(CO)_4}$ UNDER VARIOUS PARTIAL PRESSURES OF CARBON MONOXIDE
Temperature: 15°; total pressure: 1 atm.

p_{CO} (atm)	$\mathrm{HCo(CO)_4}$ ($\mathrm{mole \cdot l^{-1}}$)	$k_{\mathrm{H}}\cdot 10^4$ ($\mathrm{l \cdot mole^{-1} \cdot sec^{-1}}$)	$k_2\cdot K\cdot 10^6$ ($\mathrm{l \cdot atm \cdot mole^{-1} \cdot sec^{-1}}$)
0.688	0.860	0.153	10.5
0.670	0.876	0.187	12.5
0.473	0.439	0.217	10.2
0.467	0.582	0.273	12.7
0.467	0.591	0.214	10.0
0.467	0.442	0.233	10.9
0.236	0.362	0.440	10.4
0.233	0.364	0.452	10.5
0.154	0.321	0.687	10.6
0.136	0.278	0.664	10.3
0.095	0.244	1.00	9.5

When the experiments were started under nitrogen or hydrogen, the existence of equilibrium (1) resulted in the rapid evolution of a small amount of carbon monoxide. The p_{CO} and the concentration of $\mathrm{HCo(CO)_3}$ thus formed were determined by the gas/liquid ratio in the reaction flask.

$$K=\frac{[\mathrm{HCo(CO)_3}]\cdot p_{\mathrm{CO}}}{[\mathrm{HCo(CO)_4}]}=\frac{V_{\mathrm{G}}\cdot p_{\mathrm{CO}}^2}{V_t\cdot V_{\mathrm{F}}\cdot[\mathrm{HCo(CO)_4}]} \tag{7}$$

$$p_{\mathrm{CO}}=K\cdot V_t\cdot\frac{V_{\mathrm{F}}}{V_{\mathrm{G}}}\cdot[\mathrm{HCo(CO)_4}]=A\cdot\frac{V_{\mathrm{F}}}{V_{\mathrm{G}}}\cdot[\mathrm{HCo(CO)_4}] \tag{8}$$

where

V_{G} and V_{F} = volume of the gas and liquid phase, respectively (1)
V_t = molar volume of gas at temperature t ($\mathrm{l \cdot atm \cdot mole^{-1}}$)
$A = K\cdot V_t$ = constant

It follows from eqn. (6), that constant values of k_{H} can only be expected after a correction for p_{CO}. Using eqn. (6) and (8), relationship (9) can be derived.

$$k_{\mathrm{H}}\cdot\frac{V_{\mathrm{F}}}{V_{\mathrm{G}}}\cdot[\mathrm{HCo(CO)_4}]=\frac{k_2\cdot K}{A} \tag{9}$$

The validity of this relationship is illustrated by the experimental results in Table 3.

TABLE 3

RATE OF DECOMPOSITION OF $HCo(CO)_4$ IN HYDROGEN AT DIFFERENT V_G/V_F RATIOS
Temperature: 15°; total pressure: 1 atm.

$[HCo(CO)_4]$ (mole·l^{-1})	$\frac{V_G}{V_F}$	$k_H \cdot 10^4$ (l·mole^{-1}·sec^{-1})	$\frac{k_2 \cdot K}{A} \cdot 10^5$
0.454	49.2	16.7	16.1
0.518	48.7	15.6	16.1
0.286	36.3	18.8	16.7
0.529	22.4	10.5	16.1
0.291	16.6	12.3	16.3
0.279	16.6	12.3	16.0
0.291	10.3	9.63	16.2
0.293	10.3	9.57	16.1
0.291	5.14	6.52	15.5
0.535	4.30	4.38	15.5

From the values of $k_2 \cdot K$ (Table 2) and k_H (Table 3), the carbon monoxide partial pressures built up during the experiments under hydrogen can be calculated. This permits determination of K with the help of eqn. (7), and thus k_2 can be derived. These measurements and calculations were also performed at 20 and 25°, and Table 4 gives the values of k_2 and K, determined at all the three temperatures. The data were used to calculate the thermodynamic and activation parameters of reactions (1) and (2):

TABLE 4

EQUILIBRIUM CONSTANT K OF REACTION (1) AND REACTION VELOCITY CONSTANT k_2 OF REACTION (2) AT DIFFERENT TEMPERATURES

Temp. (°C)	$K \cdot 10^4$ (atm)	$k_2 \cdot 10^2$ (l·mole^{-1}·sec^{-1})
15	1.9	5.8
20	2.6	7.6
25	4.0	11.4

reaction (1) $\Delta H = 13000$ cal·mole^{-1}
$\Delta S = 29$ e.u.
reaction (2) $\Delta H^{\neq} = 11000$ cal·mole^{-1}
$\Delta S^{\neq} = -26$ e.u.

Experiments were carried out with $DCo(CO)_4$ at 15° to determine the overall reaction velocity constant of reaction (10). Using eqn. (11) it was shown that the ratio of k_H to k_D varies between 1.14/1 and 1.20/1.

$$2\,DCo(CO)_4 \xrightarrow{k_D} D_2 + Co_2(CO)_8 \tag{10}$$

$$-\frac{d[DCo(CO)_4]}{dt} = k_D \cdot [DCo(CO)_4]^2 \tag{11}$$

DISCUSSION

The decomposition of cobalt tetracarbonyl hydride to dicobalt octacarbonyl and hydrogen in n-heptane was found to be a well reproducible reaction, in contrast to the results achieved in gas phase experiments[1-3]. The difficulties in the latter case are most probably due to the enhanced influence of heterogeneous surfaces in the gas phase.

The rate determining step is, as could be expected, the bimolecular reaction (2) of two mononuclear cobalt carbonyl hydride species. Unexpected, however, was the prior formation of the coordinatively unsaturated $HCo(CO)_3$, which thus seems to be a rather general intermediate in the reactions of $HCo(CO)_4$. Apparently, the dimerization of the two mononuclear species needs the participation of a vacant coordination site and a vacant orbital on one of the cobalt atoms.

The available data do not enable much to be said about the intermediate $H_2Co(CO)_7$ formed in reaction (2). Since two isomers of $Co_2(CO)_8$ exist in solution[9,10], $H_2Co(CO)_7$ may also exist as several isomers and this could play a significant role in the pathway necessary for the combination of the two hydrogen atoms. The lack of a kinetic isotope effect if H is replaced by D shows, that it is not the rupture of cobalt–hydrogen bonds, which is rate determining. The activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ fall within those limits, which are characteristic for bimolecular reactions.

The determination of the equilibrium constant K of reaction (1) is the first proof of the existence of $HCo(CO)_3$. Moreover, the values of K show that the concentration of this unsaturated species is not extremely small (a few tenths of a per cent at 1 atm p_{CO} and around 20°). It is of interest to calculate its concentration under the usual conditions of hydroformylation (150° and 100 atm p_{CO}), with the aid of the thermodynamic parameters ΔH and ΔS. The result (0.3% of the concentration of $HCo(CO)_4$) is only very approximate, since it involves a large extrapolation, but its order of magnitude seems to be realistic for an intermediate of such high reactivity. This means, that $HCo(CO)_3$ can be regarded as a probable intermediate in hydroformylation and recent scepticism about its existence[11] is perhaps unjustified.

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