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THERMAL, PHOTOCHEMICAL AND ALCOHOL CATALYZED FORMATION OF $Co_4(CO)_{12}$ FROM $Co_2(CO)_8$. KINETICS AND MECHANISM

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Summary

The kinetics of formation of $Co_4(CO)_{12}$ from $Co_2(CO)_8$ in n-heptane are complex and dependent on the reaction conditions (e.g. argon flow rate). The most probable reaction order is 0.5 and the activation energy <50 kJ/mol. The reaction is enhanced by UV light ($\phi \leqslant 0.01$) and addition of small amounts of ethanol. The reaction mechanism is discussed in terms of a chain reaction with $HCo(CO)_4$ or $Co(CO)_4$ as a chain carrier and/or pathway via $Co_2(CO)_7$.

Introduction

Despite the importance of cobalt carbonyls for catalytic reactions and recent interest in metal carbonyl clusters as homogeneous models of heterogeneous catalysts, only a few quantitative studies of the formation of tetracobaltdodecacarbonyl from dicobaltoctacarbonyl (eq. 1) have been published (Table 1).

$$2\ Co_2(CO)_8 \xrightarrow{20-80^\circ C} Co_4(CO)_{12} + 4\ CO \qquad (1)$$

The available information on the kinetics and the mechanism is somewhat conflicting and sometimes confusing, as the summary in Table 1 shows. Most authors agree that $Co_4(CO)_{12}$ is formed from $Co_2(CO)_8$ at temperatures from 20—80°C. At higher temperatures decomposition of $Co_4(CO)_{12}$ occurs (eq. 2) [1,3].

$$Co_4(CO)_{12} \xrightarrow{>100^\circ C} 4\ Co + 12\ CO \qquad (2)$$

TABLE 1

PREVIOUSLY REPORTED KINETIC DATA FOR THE CONVERSION AND DECOMPOSITION OF $Co_2(CO)_8$

E_a (kJ/mol)	Reaction order (n)	remarks	ref.
		Conversion to $Co_4(CO)_{12}$	
59	2	in heptane, via $Co_2(CO)_7$ and $Co_2(CO)_6$	5
		Argon flow enhances reaction, via $Co_2(CO)_7$	8
		UV light enhances reaction	11, 12
		gamma irradiation inhibits reaction	12
		Decomposition to Co	
51	1	$Co_2(CO)_8$ decomposition in alcohol	9
47	1	$Co_2(CO)_8$ decomposition in toluene	9
61		gas phase via $^{\cdot}Co(CO)_4$	6
15		$Co_2(CO)_8$ decomposition at 140—345°C catalyzed by Co powder, inhibited by CO gas	10
		Other investigations	
		$Co_2(CO)_8 + 2[Co(ROH)]_6][Co(CO)_4]_2 \rightarrow$ $2\ Co_4(CO)_{12} + 12\ ROH$	13
		UV irradiation of $Co_2(CO)_8$ in an Ar matrix yields $Co_2(CO)_7$ at 350 nm and $^{\cdot}Co(CO)_4 + Co_2(CO)_7$ at 254 nm	17
		On active Co surfaces $^{\cdot}Co(CO)_4$ and $Co_2(CO)_6$ are formed	17

The condensation of two molecules of $Co_2(CO)_8$ to give $Co_4(CO)_{12}$ + 4 CO is endothermic by 138 kJ/mol (determined by equilibrium measurements) or 213 kJ/mol (calculated via ΔH_f^0) [4]. However, the reaction is possible due to a high increase in entropy ($T\Delta S^0$ is ca. 30—34 kJ/mol CO evolved) [4].

In this paper we report reasons for the discrepancies in the activation parameters of reaction 1 and speculate about the mechanism of $Co_4(CO)_{12}$ formation.

Experimental

Chemicals. All solvents were commercial spectrograde products (Uvasol, Merck) and were dried and flushed with argon before use. $Co_2(CO)_8$ was prepared from CO^{II} acetate [14] and recrystallized from CH_2Cl_2 and hexane at low temperature before use. $Co_4(CO)_{12}$ was prepared by refluxing $Co_2(CO)_8$ in cyclopentane [15].

The conversion of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ was carried out in a thermostated 200 ml flask equipped with stirrer, reflux condenser, thermometer, argon inlet with flow control and a rubber cap to allow sampling during the reaction. 120 ml of n-heptane were placed into the flask, which was flushed with argon and thermostated at the desired temperature. Solid $Co_2(CO)_8$ was added, and dissolved within 2 minutes. At appropriate intervals 1 ml samples of the solution were removed through a rubber cap with a syringe and immediately cooled to —70°C. The $Co_2(CO)_8/Co_4(CO)_{12}$ ratio was determined quantitatively by IR spectroscopy [11,16] (Zeiss IMR 20 spectrometer). The reactions with C_2H_5OH, THF and DMF were followed by IR, the band at 1920 cm^{-1} being characteristic for $[Co(CO)_4]^-$.

TABLE 2

INFLUENCE OF EXPERIMENTAL CONDITIONS ON THE CONVERSION OF $Co_2(CO)_8$ TO $Co_4(CO)_{12}$

Conditions: 2.5×10^{-3} mol/l $Co_2(CO)_8$ in n-heptane, 37°C

Ar flow rate (ml/min)	reaction rate (mol/l min)	"apparent" reaction order
0	7×10^{-7} [a]	0
0	1×10^{-6} [b]	0
10	8×10^{-6} [b]	0.5
100	2×10^{-5} [b]	1.2
300	4×10^{-5} [b]	1.0

[a] Small stirring bar. [b] Large stirring bar.

Results

Rates. It must first be noted that the measured rates of formation of the $Co_4(CO)_{12}$ depend on such incidentical experimental variables such as the stirring efficiency and argon flow rate (Table 2). The rates increase sharply by a factor of 40 when the Ar flow rate is changed from 0 to 300 ml/min and all other factors are kept constant.

Reaction order. The apparent reaction order, as determined from the plots of concentration against time by the fractional life method, also depends strongly on the experimental conditions. Thus, using an initial $Co_2(CO)_8$ concentration of 2.5×10^{-3} mol/l, the internal order changes from 0 *to* 1 with increasing Ar flow (Table 2). Under certain conditions the apparent order may even vary from 0 to 3, depending on the temperature (Table 3). The true reaction order, as determined by the concentration dependence of the $Co_4(CO)_{12}$ formation, however, was found to be ~0.5 (Table 4).

Activation energy. Similar variations with the reaction conditions were found

TABLE 3

REACTION RATES FOR THE CONVERSION OF $Co_2(CO)_8$ TO $Co_4(CO)_{12}$ AT DIFFERENT TEMPERATURES IN n-HEPTANE

Temp. (°C)	reaction rate (mol/l min)	"apparent" reaction order	remarks
37	1×10^{-6}	0 [a]	$c_0 = 2.5 \times 10^{-3}$ mol/l [b]
50	7×10^{-6}	3.2	Ar flow rate = 0 ml/min
65	49×10^{-6}	2.8	$E_a = 121$ kJ/mol
11	2×10^{-6}	1.8	$c_0 = 2.5 \times 10^{-3}$ mol/l [b]
17	4×10^{-6}	1	Ar flow rate = 100 ml/min
25	9×10^{-6}	1	$E_a = 71$ kJ/mol
37	27×10^{-6}	1	
25	14×10^{-6}	0.35 [a]	$c_0 = 1 \times 10^{-2}$ mol/l [b]
37	28×10^{-6}	0.37	Ar flow rate ≈80 ml/min
50	70×10^{-6}	0.8	$E_a = 50$ kJ/mol

[a] With induction period. [b] c_0 = starting concentration of $Co_2(CO)_8$.

TABLE 4

INFLUENCE OF INITIAL $Co_2(CO)_8$ CONCENTRATION ON THE FORMATION OF $Co_4(CO)_{12}$ IN n-HEPTANE

c_0 [a] (mol/l)	reaction rate (mol/l mol)	"true" reaction order	remarks
2.5×10^{-3}	1.7×10^{-5}	0.4	37°C
5×10^{-3}	1.8×10^{-5}		Ar flow rate ≈80 ml/min
10×10^{-3}	2.5×10^{-5}		
2.5×10^{-3}	6.3×10^{-6}	0.6	25°C
10×10^{-3}	14×10^{-6}		Ar flow rate ≈80 ml/min

[a] c_0 = starting concentration of $Co_2(CO)_8$.

for the Arrhenius activation energies, which varied between 50 and 120 kJ/mol. Most experiments, however, resulted in E_a values of about 50 to 71 kJ/mol (Table 3). UV light increases the reaction rates moderately with quantum yields of $\phi = 10^{-3}$ to 10^{-2} (Table 5) as previously noted [11,12].

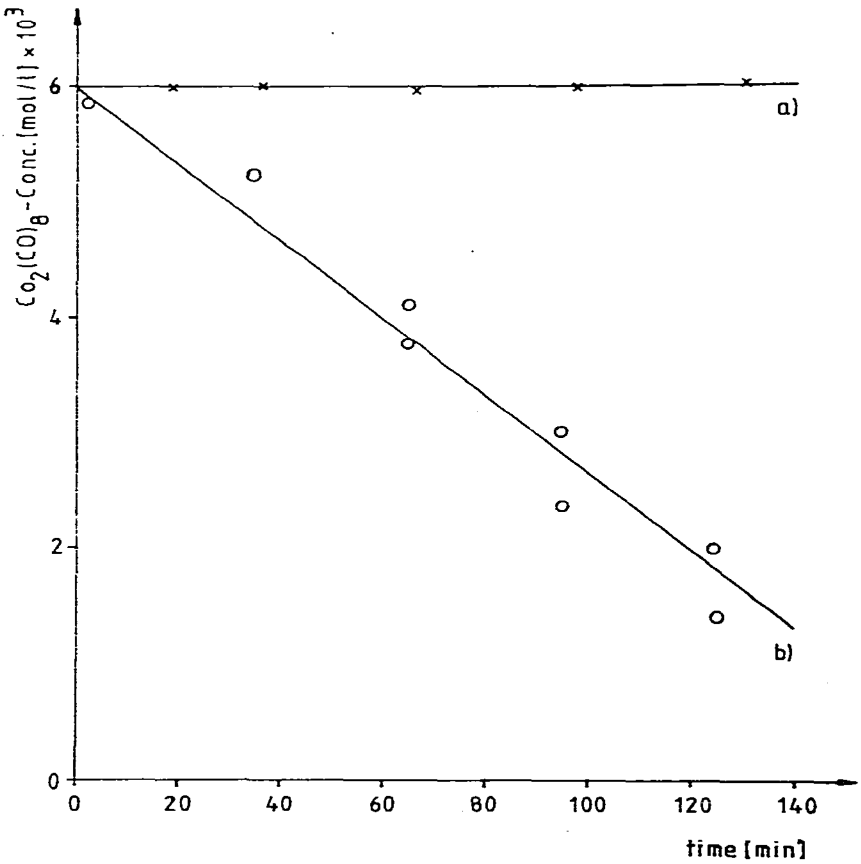

Fig. 1. Effect of ethanol on the conversion of $Co_2(CO)_8$ to $Co_4(CO)_{12}$. a) 6×10^{-3} mol/l $Co_2(CO)_8$ in n-heptane; b) solution a) +0.06 mol/l ethanol.

TABLE 5

PHOTOCHEMICAL CONVERSION OF $Co_2(CO)_8$ TO $Co_4(CO)_{12}$

Conditions: 2.5×10^{-3} mol/l $Co_2(CO)_8$ in n-heptane, 700 W Hg lamp (Hanau).

Temp. (°C)	reaction rates (mol/l min)		remarks
	photo [a]	thermal	
13	3×10^{-6}	0.9×10^{-6}	Ar flow rate = 50 ml/min
17	4×10^{-6}	2×10^{-6}	
25	10×10^{-6}	6×10^{-6}	
11	4×10^{-6}	2×10^{-6}	Ar flow rate = 100 ml/min
17	5×10^{-6}	4×10^{-6}	

[a] The quantum yields were ϕ (366 nm) = 10^{-3}–10^{-2}, depending on conditions.

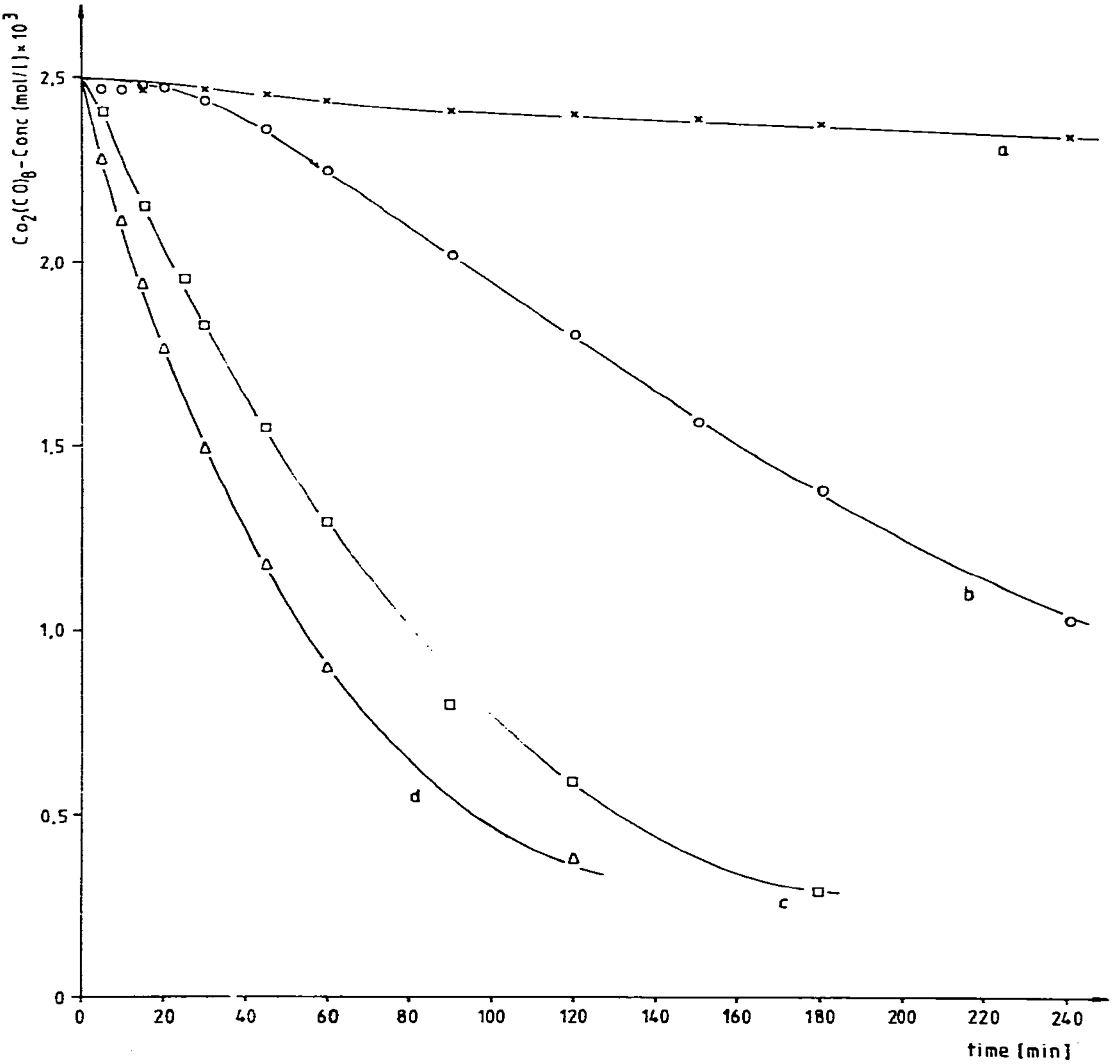

Fig. 2. Decrease of the $Co_2(CO)_8$ concentration with time at various argon flow rates. Solvent: n-heptane; temp.: 37°C; argon flow rates: 0 ml/min (a), 10 ml/min (b), 100 ml/min (c), 300 ml/min (d).

Additives. Most surprising is that the reaction rates are dramatically enhanced when a small amount of ethanol was added to the solution (Fig. 1). No enhanced $Co_4(CO)_{12}$ formation was observed when THF or DMF were added. Addition of DMF resulted in a slow decomposition of $Co_2(CO)_8$ to give unidentified products which did not contain CO groups.

Sometimes the $Co_4(CO)_{12}$ formation started only after poorly reproducable induction periods of up to 20 minutes, particularly at low temperatures or low Ar flow rates (Fig. 2). Similarly, the conversion was not always complete, but occasionally a small amount of $Co_2(CO)_8$ remained unchanged even after long reaction times.

Discussion

The divergent literature data and the experimental data in this work lead to the same conclusion: The formation of $Co_4(CO)_{12}$ from $Co_2(CO)_8$ follows a more complex mechanism than previously supposed [5]. This view is supported by:

a) The difference between the "apparent" (from concentration vrs. time plots) and the "true" reaction orders (from concentration dependence of the initial rates).

b) The differences of the reaction rates.

c) The variations in activation energies, depending on reaction conditions.

d) The non-ideal behaviour of the reaction at very low and very high conversions.

e) The influence of light on the reaction rates.

f) The influence of alcohols on the reaction rates.

These features of reaction 1 are discussed in detail below.

a) The "true" reaction order in our experiments is close to 0.5. This value points towards some type of chain reaction. The "apparent" reaction order, however, is different. At low temperature, which implies low conversions in the time of measurement, the "apparent" order is lower than 0.5 and approaches zero. At higher conversions the reaction order is larger than 0.5. That would be consistent with a reaction which is autocatalyzed at the beginning and autoinhibited at the end.

b) Higher reaction rates with increasing argon flow or stirring efficiency indicate the formation of an inhibiting substance which is removed by agitation of the solution. The most likely inhibitor is the carbon monoxide evolved during the reaction.

c) Since the apparent activation energies vary widely depending on the experimental conditions, it seems logical to assume that the measured values are determined by a rate-limiting process which is irrelevant to the chemical mechanism; the most likely possibility is again the removal of evolved CO from the reaction system. We were not able to reach a limiting value of the rates or activation energies by optimizing experimental parameters such as Ar flow rate, stirring efficiency, concentration etc. Therefore, it must be assumed that the lowest value of E_a, ≈ 50 kJ/mol, is still an "artificial" value caused by physical effects, and that the "true" chemical reaction which leads eventually to $Co_4(CO)_{12}$ has a still lower activation energy. Similar effects were observed by

Baev et al. On investigating the thermal decomposition of solid $Co_2(CO)_8$ [10] and $Co_4(CO)_{12}$ [2] they observed different values of E_a depending on the conditions. An E_a value of 16 kJ/mol extrapolated to complete removal of CO [10] would be consistent with our experiments, although we could not confirm it, and with CO exchange data [19]. Under certain conditions (Table 3) we were able to reproduce the E_a values of 45—60 kJ/mol obtained by other authors (Table 1), we do not, however, consider them to refer to a true chemical reaction but link it to a CO transportation phenomenon.

d) The observed induction periods and the non-ideal behaviour at high conversion are consistent with autocatalytic and autoinhibition mechanisms, as discussed under a).

e) It is noteworthy that although UV irradiation enhances $Co_4(CO)_{12}$ formation, the quantum yield for this process is very small. Matrix studies [17] suggest that the primary photochemical step is the formation of $Co_2(CO)_7$ (eq. 3) or $Co(CO)_4$ (eq. 4). The inefficiency of these reactions could be accounted for by a thermal back reaction of $Co_2(CO)_7$ with CO within the solvent cage or facile recombination of two $Co(CO)_4$ radicals (eq. 4).

$$Co_2(CO)_8 \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} Co_2(CO)_7 + CO \qquad (3)$$

$$Co_2(CO)_8 \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} 2\,{}^{\cdot}Co(CO)_4 \qquad (4)$$

A charge transfer excitation producing ionic intermediates according to equation 5 also seems feasible.

$$Co_2(CO)_8 \xrightarrow{\Delta \text{ or } h\nu} [Co(CO)_4]^+ + [Co(CO)_4]^- \qquad (5)$$

f) Most surprising is the catalytic effect of added alcohol on $Co_4(CO)_{12}$ formation. Although there are two reports in the literature on the influence of isopropanol and higher alcohols on the equilibrium 1 [4,13,20], it has not previously been observed that even a small concentration of a simple alcohol such as ethanol suffices to convert $Co_2(CO)_8$ to $Co_4(CO)_{12}$ without any detectable formation of the normal [20] disproportionation product $[Co(ROH)_6]$-$[Co(CO)_4]_2$ (eq. 6). This latter product is observed, however, when a large concentration of ethanol is present in the solution (eq. 7).

Aprotic Lewis bases such as tetrahydrofuran and dimethylformamide in similar concentrations did not enhance the $Co_4(CO)_{12}$ formation under our conditions. This suggests that protons are responsible for the "alcohol-effect".

$$2\ Co_2(CO)_8 \xrightarrow[\text{low conc.}]{\text{ethanol}} Co_4(CO)_{12} + 4\ CO \qquad (6)$$

$$3\ Co_2(CO)_8 \xrightarrow[\text{high conc.}]{\text{ethanol}} 2[Co(EtOH)_6][Co(CO)_4]_2 \qquad (7)$$

A reaction sequence of the type shown in equations 8—11 would explain not only the alcohol-catalyzed formation of $Co_4(CO)_{12}$ but also most of the

$$Co_2(CO)_8 \rightleftharpoons [Co(CO)_4]^+ + [Co(CO)_4]^- \qquad (8)$$

$$H^+ + [Co(CO)_4]^- \rightleftharpoons HCo(CO)_4 \qquad (9)$$

$$HCo(CO)_4 + Co_2(CO)_8 \rightleftharpoons HCo_3(CO)_{10} + 2\ CO \qquad (10)$$

$$2\ HCo_3(CO)_{10} \rightleftharpoons Co_4(CO)_{12} + 2\ HCo(CO)_4 \qquad (11)$$

observed effects in the thermal and photochemical reaction. Only the formation (eq. 9) of $HCo(CO)_4$ need be replaced by a non-ionic path, e.g. eq. 12 and 13.

$$Co_2(CO)_8 \rightleftharpoons 2\ {}^{\cdot}Co(CO)_4 \qquad (12)$$

$$^{\cdot}Co(CO)_4 + R{-}H \rightleftharpoons HCo(CO)_4 + R^{\cdot} \qquad (13)$$

The hydrogen abstraction step (eq. 13) is not even necessary to explain the formation of $Co_4(CO)_{12}$. A chain reaction via radicals is also feasible (eq. 14, 15) *.

$$^{\cdot}Co(CO)_4 + Co_2(CO)_8 \rightleftharpoons {}^{\cdot}Co_3(CO)_{10} + 2\ CO \qquad (14)$$

$$^{\cdot}Co_3(CO)_{10} + Co_2(CO)_8 \rightleftharpoons Co_4(CO)_{12} + {}^{\cdot}Co(CO)_4 + 2\ CO \qquad (15)$$

Beside these two variations of a chain mechanism a CO extrusion in the first step to give eventually $Co_2(CO)_6$ (eq. 16) as suggested by the photochemical experiments and some literature data [5,7,9] is a possible alternative.

$$Co_2(CO)_8 \xrightarrow{-CO} Co_2(CO)_7 \xrightarrow{-CO} Co_2(CO)_6 \qquad (16)$$

A second order reaction of two $Co_2(CO)_6$ fragments to give $Co_4(CO)_{12}$, as proposed by Ungvary und Markó [5], is not, however, supported by our experiments, and it seems indeed very improbable that two 14 electron species survive long enough under the reaction conditions to react with each other. If a $Co_2(CO)_6$ species is formed, it is likely to react with $Co_2(CO)_8$ perhaps as indicated in eq. 17.

$$Co_2(CO)_6 + Co_2(CO)_8 \rightarrow Co_4(CO)_{12} + 2\ CO \qquad (17)$$

$Co_4(CO)_{12}$ itself is another possible source of $Co_2(CO)_6$ (eq. 18), which could account for the autocatalytic nature of the reaction.

$$Co_4(CO)_{12} \rightleftharpoons 2\ Co_2(CO)_6 \qquad (18)$$

On the basis of the available data it is difficult to decide which mechanism operates in the thermal $Co_4(CO)_{12}$ formation. It may be that two or more mechanisms occur simultaneously, the dominating pathway being determined by the reaction conditions. For the alcohol assisted reaction, however, a mechanism involving ionic species via disproportionation of the $Co_2(CO)_8$ seems most likely.

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* A similar chain process was recently proposed for the decomposition of $HCo(CO)_4$ [18].

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