

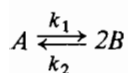
The Formation of $\text{HCo}(\text{CO})_4$ from $\text{Co}_2(\text{CO})_8$ or $\text{Co}_4(\text{CO})_{12}$. A High Pressure IR and UV Spectroscopic Study

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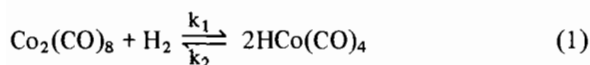
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Under high pressure tetracobalt dodecacarbonyl reacts first with CO to give dicobalt octacarbonyl. The latter reacts with H_2 to $\text{HCo}(\text{CO})_4$ via an associative or a dissociative mechanism depending on the partial pressure of CO. Reversible kinetics of the type



are applied for the equilibrium $\text{Co}_2(\text{CO})_8 + \text{H}_2 \rightleftharpoons 2\text{HCo}(\text{CO})_4$ at $P(\text{H}_2) = 45$ bar and 80°C . For $P(\text{CO}) < P(\text{H}_2)$ the rate constants depend on the partial pressure of CO. For $P(\text{CO}) \geq P(\text{H}_2)$ the rate constants are $k_1 = 0.0040 \text{ min}^{-1}$ and $k_2 = 0.10 \text{ l/mol min}$, independent of CO pressure.

The formation of $\text{HCo}(\text{CO})_4$ from cobalt carbonyl precursors is one of the most important steps in cobalt-catalyzed syn-gas reactions (eqn. 1) [1–3].



So far, only conflicting information on the mechanism of the $\text{HCo}(\text{CO})_4$ formation from $\text{Co}_2(\text{CO})_8$ is available [4–9]. An associative [4–6] and two dissociative pathways (via $\text{Co}_2(\text{CO})_7$ or $\text{Co}_2(\text{CO})_6$) have been discussed [6–8]. Other possible intermediates include $\text{H}_2\text{Co}_2(\text{CO})_8$ [5], $\text{HCo}_3(\text{CO})_9$ [10], $\text{Co}_2(\text{CO})_9$ [4, 11, 12], or $\text{Co}(\text{CO})_4$ [13, 14]. Ungvary suggests parallel dissociative and associative pathways for the $\text{HCo}(\text{CO})_4$ formation [6]. Text-books usually omit the associative part of the mechanism (e.g. [9]), and the results were questioned by an on-line high pressure IR study [7, 8].

With $\text{Co}_4(\text{CO})_{12}$ as the starting material much less information is available. The direct formation of $\text{HCo}(\text{CO})_3$ [15] and the intermediate formation of $\text{Co}_2(\text{CO})_8$ [16] have been proposed.

Some clarification of the $\text{Co}_2(\text{CO})_8$ problem could be expected by a study of the $\text{HCo}(\text{CO})_4$ formation as a function of the CO pressure.

In this paper I present direct evidence, obtained by on-line high pressure IR and UV spectroscopy,

that $\text{HCo}(\text{CO})_4$ can indeed be formed from dicobalt octacarbonyl via a dissociative and an associative mechanism, depending on the CO partial pressures. Under the conditions typical for catalytic syn-gas reactions the associative pathway dominates. Tetracobalt dodecacarbonyl is converted to $\text{HCo}(\text{CO})_4$ via the intermediate formation of $\text{Co}_2(\text{CO})_8$.

Experimental

The experiments were performed in a circulating system which allowed on-line recording of the UV and IR spectra [17]. The optical pathlength of the UV cell was 0.05 cm and that of the IR cell 0.009 cm. The high pressure cells were kept at 25°C to provide a constant ratio of the $\text{Co}_2(\text{CO})_8$ isomers with bridged and terminal CO's. This causes only negligible error since the equilibrium between $\text{Co}_2(\text{CO})_8$ and $\text{HCo}(\text{CO})_4$ changes by <1% during the time required for the solution to reach the cells (1 to 3 minutes).

In a typical run the autoclave was charged with 600 ml of argon-saturated methyl cyclohexane and 1.55 g $\text{Co}_2(\text{CO})_8$ was placed in a by-pass. The system was flushed twice with 10 bar CO, the required H_2 and CO pressures were applied, and then heated to 80°C . The by-pass was opened and the $\text{Co}_2(\text{CO})_8$ was pumped into the autoclave. At appropriate intervals the IR and UV spectra of the mixture were recorded and for quantitative analysis the optical densities of the bands were compared with a calibrated curve. The absorptivities obeyed Beer's law, but their absolute values depended on the scanning rate and other experimental conditions (compare also references [7, 8, 18]).

$\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ were prepared according to literature procedures [19, 20].

Results and Discussion

$\text{Co}_2(\text{CO})_8$: The formation of $\text{HCo}(\text{CO})_4$ from $\text{Co}_2(\text{CO})_8$ was studied at a constant pressure of hydrogen with various pressures of CO ($P(\text{H}_2) =$

TABLE I. Rate Constants for the Formation of $\text{HCo}(\text{CO})_4$ from $\text{Co}_2(\text{CO})_8$ at Various CO Pressures. Conditions: $P(\text{H}_2) = 45$ bar; $T = 80$ °C; 1.55 g $\text{Co}_2(\text{CO})_8$ ($= 7.6$ mmol/l) in 600 ml Methylcyclohexane.

$P(\text{CO})$ [bar]	k_1 [min^{-1}]	r_1° [mol/l min]	k_2 [$1/\text{mol min}$]	$r_1 = r_2$ [mol/l min]
11	0.0085	6.5×10^{-5}	0.21	2.1×10^{-5}
22	0.0045	3.4×10^{-5}	0.11	1.1×10^{-5}
45	0.0040	3.0×10^{-5}	0.10	1.0×10^{-5}
60	0.0040	3.0×10^{-5}	0.10	1.0×10^{-5}

r_1° = rate at the beginning of the $\text{Co}_2(\text{CO})_8$ conversion r_1, r_2 = rates under equilibrium conditions (67% $\text{HCo}(\text{CO})_4$)

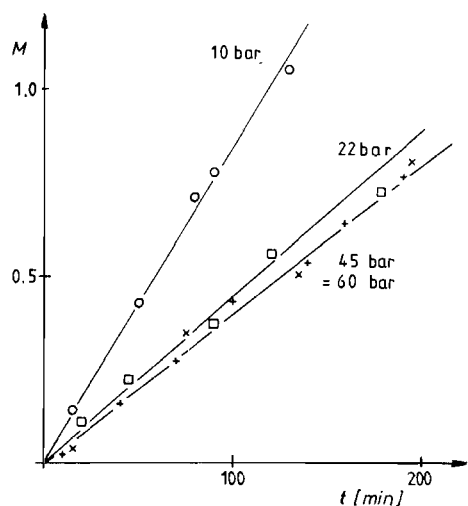


Fig. 1. Formation of $\text{HCo}(\text{CO})_4$ from $\text{Co}_2(\text{CO})_8$ as a function of time at various partial pressures of CO and a constant partial pressure of H_2 . Conditions: 1.55 g $\text{Co}_2(\text{CO})_8$ in 600 ml methyl cyclohexane ($= 0.0076$ mol/l); $P(\text{H}_2) = 40$ bar (at 25 °C); $T = 80$ °C. $P(\text{CO}) = 10$ bar (\circ); 22 bar (\square); 45 bar ($+$), 60 bar (\times). Reversible kinetics for an equilibrium $A \rightleftharpoons 2B$ were applied [23]; $M = k_1 t$, with $M = [(C_0 - C_\infty)/(C_0 + C_\infty)] - \ln[(C_0^2 - C_\infty C)/(C - C_\infty)C_0]$ C = concentration of A at time t , C_0 = initial concentration of A, C_∞ = equilibrium concentration.

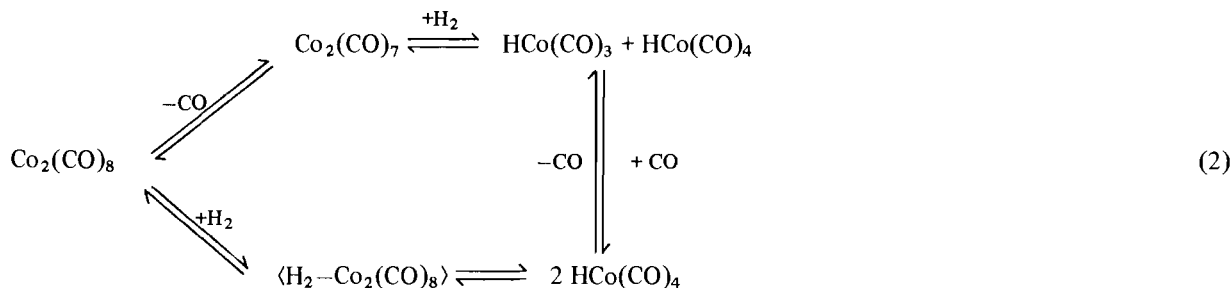
45 bar at 80 °C). The decrease of the $\text{Co}_2(\text{CO})_8$ concentration was followed by UV (350 nm) and IR (1856 cm^{-1}) spectroscopy. The $\text{HCo}(\text{CO})_4$ formation was monitored in the IR (2032 cm^{-1}). The reaction proceeds unequivocally. $\text{Co}_2(\text{CO})_8$ and $\text{HCo}(\text{CO})_4$ account for $>95\%$ of the total cobalt and

no other carbonyl species could be detected. After 24 hours (at 45 bar H_2 and 80 °C) the equilibrium containing 67% of the cobalt as $\text{HCo}(\text{CO})_4$ is reached. The equilibrium is nearly independent of CO pressure between 10 and 60 bar. It depends, however, on the H_2 pressure and on the temperature, in agreement with previous studies [4–8].

Assuming that the forward reaction of eqn. 1 is first order in $\text{Co}_2(\text{CO})_8$ and the reverse reaction second order in $\text{HCo}(\text{CO})_4$ [21, 22], and that H_2 is present in a large excess, reversible kinetics of the type $A \rightleftharpoons 2B$ can be applied to the equilibrium (Fig. 1). From the slope of the straight lines in Fig. 1 the rate constants k_1 and k_2 for the forward and back reaction can be determined (Table I) [23].

The results show that the $\text{HCo}(\text{CO})_4$ formation is inhibited by CO, but only to a limited extent. Upon increasing the CO pressure from 11 to 22 bar the rate of $\text{HCo}(\text{CO})_4$ formation drops to half the original value. A further increase to 60 bar, however, has only a very slight effect. In other words at CO partial pressures $P(\text{CO}) \geq P(\text{H}_2)$ the rate of the $\text{HCo}(\text{CO})_4$ formation is nearly independent of CO. That means $\text{HCo}(\text{CO})_4$ can be formed via two (or more) competing mechanisms: dissociative, inhibited by CO, and associative, independent of the CO pressure (eqn. 2). Our on-line experiments confirm Ungvary's earlier conclusions, derived from a more indirect off-line study [6].

No cobalt carbonyls other than $\text{Co}_2(\text{CO})_8$ and $\text{HCo}(\text{CO})_4$ were detected under the conditions used and there was no evidence that $\text{Co}(\text{CO})_4$ radicals were involved either in the forward or the back reaction,



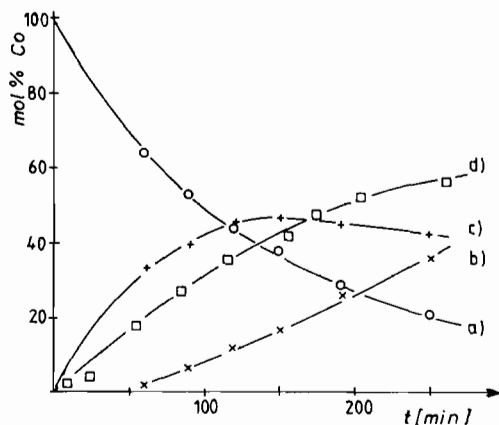
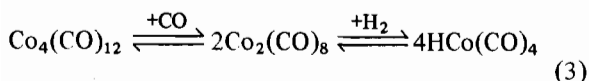


Fig. 2. Reaction of $\text{Co}_4(\text{CO})_{12}$ with synthesis gas. Plotted are the % cobalt present as a) $\text{Co}_4(\text{CO})_{12}$; b) $\text{HCo}(\text{CO})_4$; c) $\text{Co}_2(\text{CO})_8$; d) formation of $\text{HCo}(\text{CO})_4$ from $\text{Co}_2(\text{CO})_8$ under identical conditions. Conditions 1.3 g $\text{Co}_4(\text{CO})_{12}$ (= 0.0038 mol/l) or 1.55 g $\text{Co}_2(\text{CO})_8$ (= 0.0076 mol/l) in 600 ml methyl cyclohexane; P = 98 bar $\text{CO}/\text{H}_2 = 1$; T = 80 °C.

as was found previously in photochemical experiments [13, 14].

For the hydroformylation or other cobalt catalyzed syn-gas reactions usually a gas mixture with $\text{CO}/\text{H}_2 = 1$ is used. This corresponds approximately to a 2:1 excess of CO over H_2 concentration in the liquid phase (e.g. 0.5 mol/l CO and 0.25 mol/l H_2 at 80 °C and 45 bar each) [8]. Therefore the conclusion seems justified that under the conditions typical for catalytic syn-gas reactions the $\text{HCo}(\text{CO})_4$ is predominately formed via an associative pathway and therefore unaffected by CO.

$\text{Co}_4(\text{CO})_{12}$: The conversion of $\text{Co}_4(\text{CO})_{12}$ to $\text{HCo}(\text{CO})_4$ was also followed by IR and UV spectroscopy. The results shown in Fig. 2 demonstrate that at the beginning of the reaction $\text{Co}_2(\text{CO})_8$ (curve c) is formed at a rate corresponding to the decrease of $\text{Co}_4(\text{CO})_{12}$ (curve a). Only when a considerable fraction of the cobalt is present as dicobalt octacarbonyl, the $\text{HCo}(\text{CO})_4$ (curve b) appears. This means that the tetranuclear carbonyl is first converted to the dinuclear species, which then reacts further to give the cobalt carbonyl hydride (eqn. 3).



After 24 hours no $\text{Co}_4(\text{CO})_{12}$ is left and a typical equilibrium mixture with 67% and 33% of the cobalt present as $\text{HCo}(\text{CO})_4$ and $\text{Co}_2(\text{CO})_8$ respectively is observed.

A possible pathway by which the $\text{Co}_4(\text{CO})_{12}$ would be directly converted to $\text{HCo}(\text{CO})_3$ is negligible under the conditions of this experiment. For comparison a plot of the formation of $\text{HCo}(\text{CO})_4$ from $\text{Co}_2(\text{CO})_8$ is included in Fig. 2 (curve d), which shows that $\text{Co}_2(\text{CO})_8$ reacts faster than $\text{Co}_4(\text{CO})_{12}$.

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