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Preliminary communication

Low temperature activation of molecular hydrogen in CO/H_2 mixtures in the presence of $CoRh(CO)_7$

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Abstract

Molecular hydrogen (0.8–8 bar) reacts with $CoRh(CO)_7$ at 0 °C in the presence of 2 bar carbon monoxide in n-hexane to yield $HCo(CO)_4$ and $Rh_4(CO)_{12}$. When a solution of $CoRh(CO)_7$ (10^{-3} mmol/l) and 3,3-dimethyl-1-butene (0.2 mol/l) in n-hexane is treated with 2 bar carbon monoxide and 8 bar hydrogen at 0 °C, the catalytic formation of 4,4-dimethylpentanal is observed (25% conversion after 24 h). Although the reaction path of the molecular hydrogen activation is not known, the formation of an unobserved intermediate such as $\{H_2CoRh(CO)_7\}$, and its subsequent fragmentation to give $HCo(CO)_4$ and a very unstable hydridorhodium species such as $\{HRh(CO)_3\}$ rapidly yielding $Rh_4(CO)_{12}$ seems likely. The results show that low temperature activation of molecular hydrogen can be achieved at 0 °C even in the presence of substantial concentrations of carbon monoxide using $CoRh(CO)_7$.

The activation of molecular hydrogen in the presence of carbon monoxide is one of the most important steps in various catalytic reactions [1]. Of the several mechanisms proposed for hydrogen activation in homogeneous phase [2], that of the oxidative addition of H_2 has been examined in detail [3]. In this case the crucial step is the formation of a coordinatively unsaturated species preceding the hydrogen addition [4]. However, in the absence of a good leaving group ($L = PR_3$, $P(OR)_3$) and in the presence of carbon monoxide at low temperature, equilibrium (1)

$$ML_x(CO)_y \rightleftharpoons ML_x(CO)_{y-1} + CO \qquad (1)$$

is generally shifted to the left, resulting in the low concentration of a coordinatively unsaturated species and hence in slow H_2 activation, if any. We now report our observations on the low temperature reaction of molecular hydrogen with the coordinatively unsaturated compound $CoRh(CO)_7$ [5].

We recently isolated and characterized the coordinatively unsaturated $CoRh(CO)_7$

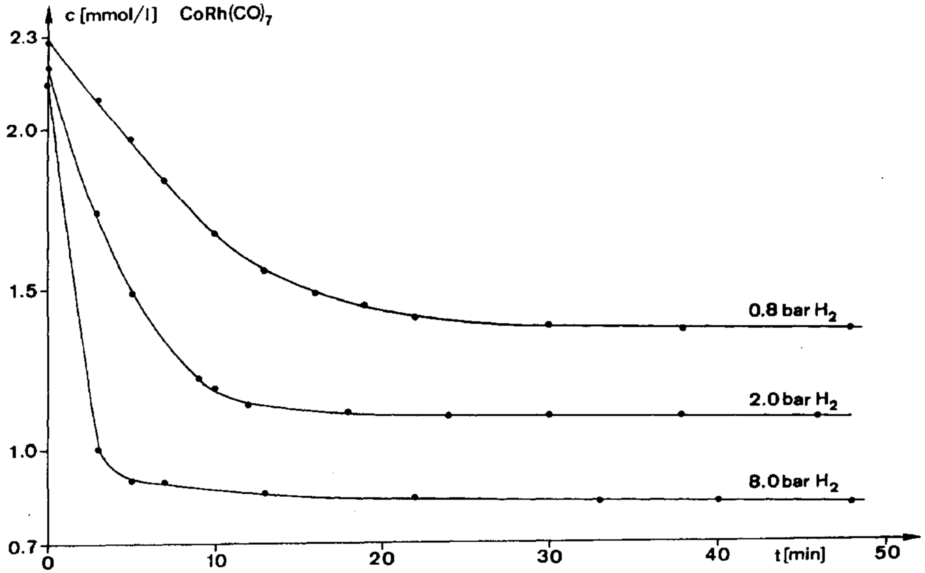

Fig. 1. Decrease of CoRh(CO)$_7$ concentration with time at different H_2 partial pressures. Reaction conditions: $T = 0\,°C$, solvent n-hexane, CO pressure 2 bar, Initial [CoRh(CO)$_7$] = 2.5 mmol/l.

[5], which is stable below 15 °C in the presence of at least 2 bar of CO. CoRh(CO)$_7$ readily reacts with molecular hydrogen (0.8–8 bar) in the presence of 2 bar carbon monoxide at 0 °C leading eventually to HCo(CO)$_4$ and Rh$_4$(CO)$_{12}$. Under 8 bar of H_2 the concentration of CoRh(CO)$_7$ falls rapidly in the first 5 min (Fig. 1), during which we observed the formation of HCo(CO)$_4$ and Rh$_4$(CO)$_{12}$. The transient formation of an unidentified species {X}, which reaches a maximum concentration after 7 minutes, was also detected (Fig. 2). Within the next 5 h, {X} disappeared and the mixture contained only CoRh(CO)$_7$, HCo(CO)$_4$ and Rh$_4$(CO)$_{12}$. Upon further stirring (20 h), there was a slow decrease in the concentration of CoRh(CO)$_7$ and HCo(CO)$_4$, an increase of Rh$_4$(CO)$_{12}$, and slow formation of Co$_2$(CO)$_8$.

At lower pressure of H_2 (2 and 0.8 bar), similar products are formed, but the disappearance of CoRh(CO)$_7$ is slower and the relative concentrations of the various species in solution are different. The fact that at different H_2 pressures CoRh(CO)$_7$, HCo(CO)$_4$, and Rh$_4$(CO)$_{12}$ approach different concentrations implies that the reaction of CoRh(CO)$_7$ and H_2 is reversible (eq. 2).

$$4\,\mathrm{CoRh(CO)_7} + 2\,\mathrm{H_2} \rightleftharpoons 4\,\mathrm{HCo(CO)_4} + \mathrm{Rh_4(CO)_{12}} \quad (2)$$

However, the relative concentration of the different species in solution slowly changes because HCo(CO)$_4$ slowly transforms to Co$_2$(CO)$_8$, and the reverse reaction of Co$_2$(CO)$_8$ with H_2 is extremely slow under the conditions used (eq. 3) [6].

$$2\,\mathrm{HCo(CO)_4} \rightleftharpoons \mathrm{Co_2(CO)_8} + \mathrm{H_2} \quad (3)$$

To find out whether the reaction between CoRh(CO)$_7$ and H_2 is reversible we treated HCo(CO)$_4$ with Rh$_4$(CO)$_{12}$ under 2 bar CO and 0.8 bar H_2 at 0 °C. Under these conditions slow formation of CoRh(CO)$_7$ was in fact observed but the relative concentrations of the metal carbonyls found in reaction (2) could not be reached, as was expected since the concurrent transformation of HCo(CO)$_4$ to Co$_2$(CO)$_8$ and H_2 occurs at a comparable rate (Figure 3). There was no spectroscopic evidence for

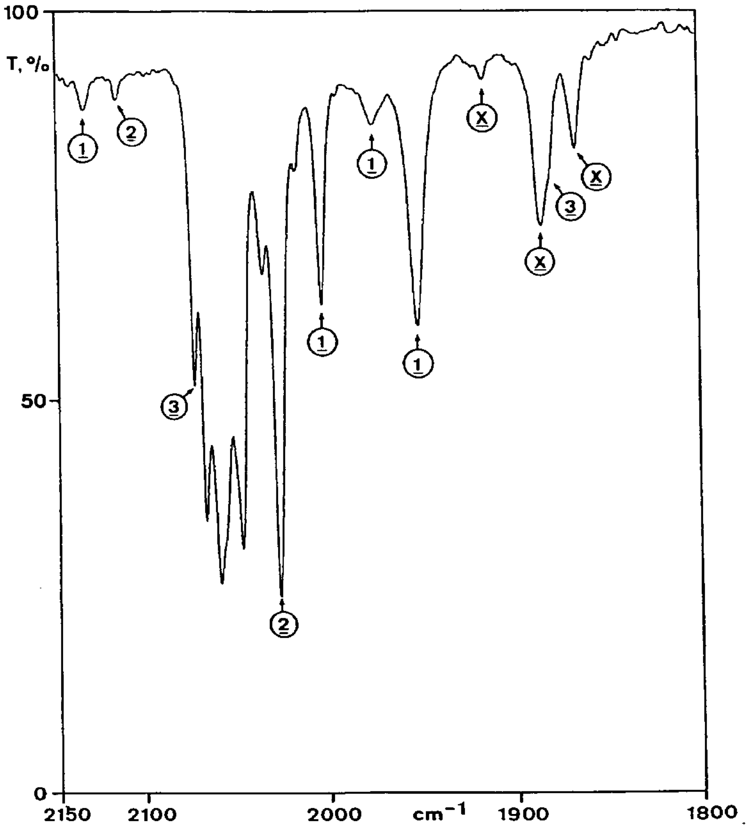

Fig. 2. IR spectrum of the ν(CO) region of the n-hexane solution with initial [$CoRh(CO)_7$] = 2.5 mmol/l, 7 minutes after the introduction of hydrogen. p_{CO} = 2 bar, p_{H_2} = 8 bar, Temperature = 0 ° C. Bands of $CoRh(CO)_7$ (**1**), $HCo(CO)_4$ (**2**), $Rh_4(CO)_{12}$ (**3**), Unidentified species (**X**).

the formation of {X} in this new synthesis of $CoRh(CO)_7$. It should be also noted here that no formation of either $CoRh(CO)_7$ or $HCo(CO)_4$ could be detected when a n-hexane solution of $Rh_4(CO)_{12}$ and $Co_2(CO)_8$ was stirred under 2 bar CO and 8 bar H_2 at 9 ° C for 24 h.

Evidence for the facile, low temperature H_2 activation was obtained by the catalytic hydroformylation of 3,3-dimethyl-1-butene using $CoRh(CO)_7$ as catalyst precursor. When a solution of $Co_2Rh_2(CO)_{12}$ (10^{-3} mmol/l) and 3,3-dimethyl-1-butene (0.2 mol/l) in n-hexane was treated with 2 bar CO at 0 ° C, $CoRh(CO)_7$ was formed in accord with equilibrium (4). When the autoclave was charged with 8 bar of H_2

$$Co_2Rh_2(CO)_{12} + 2\ CO \rightleftharpoons 2\ CoRh(CO)_7 \qquad (4)$$

4,4-dimethyl-pentanal was formed (25% conversion after 24 h). This contrasts sharply with the observation that pure $HCo(CO)_4$, $Co_2(CO)_8$, or $Rh_4(CO)_{12}$ show very little, if any, catalytic activity under these conditions. Only traces of aldehyde were found in the presence of $HCo(CO)_4$, no reaction took place when $Co_2(CO)_8$ was used, and 1% conversion was observed in the presence of $Rh_4(CO)_{12}$ after 24 h.

In view of the fact that $HCo(CO)_4$ was the only hydrogen-containing species at the end of the reaction of $CoRh(CO)_7$ and H_2, several experiments were performed

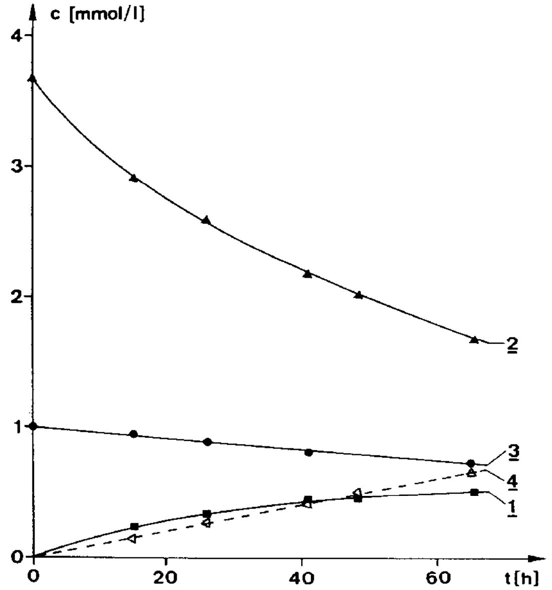

Fig. 3. Variation of the concentration of the different species formed starting with $HCo(CO)_4$ and $Rh_4(CO)_{12}$ in n-hexane as a function of time. Reaction conditions: solvent n-hexane, initial [$HCo(CO)_4$ (2)] = 3.6 mmolar, initial [$Rh_4(CO)_{12}$ (3)] = 1 mmol, under 2 bar CO, 0.8 bar H_2 at 0 °C. $CoRh(CO)_7$ (1), $Co_2(CO)_8$ (4).

to rule out activation of H_2 by $Co_2Rh_2(CO)_{12}$. Kinetic studies were carried out at 0 °C in n-hexane on the reactions: [a] of $Co_2Rh_2(CO)_{12}$ with CO ($p_{CO} = 1.70$ bar) in the absence of H_2; [b] of $CoRh(CO)_7$ with hydrogen ($p_{H_2} = 0.65$ bar, in the presence of 1.70 bar CO to ensure its stability); and [c] of $Co_2Rh_2(CO)_{12}$ upon simultaneous addition of CO and H_2 ($p_{CO} = 1.70$ bar, $p_{H_2} = 0.65$ bar).

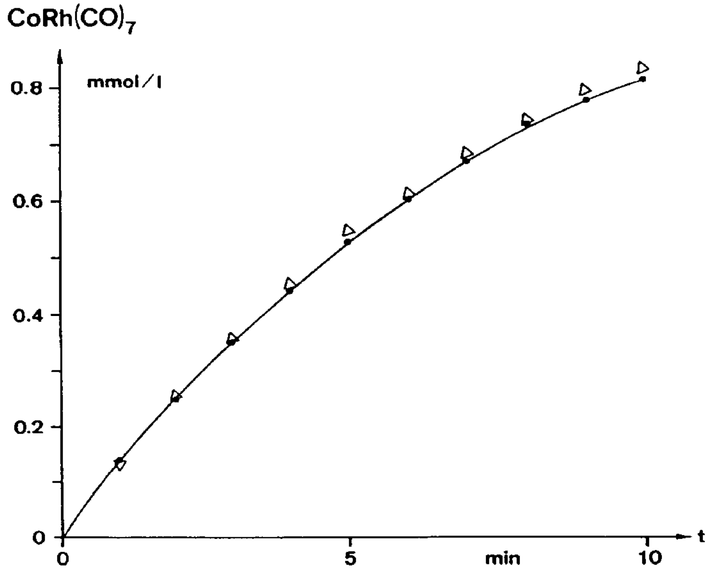

Fig. 4. Formation of $CoRh(CO)_7$ from $Co_2Rh_2(CO)_{12}$ under 1.70 bar CO, 0.65 bar H_2 at 0 °C in n-hexane as a function of time. (● experimentally measured, △ calculated assuming that $Co_2Rh_2(CO)_{12}$ reaction with H_2 is negligible).

In the reaction of $Co_2Rh_2(CO)_{12}$ with CO (experiment [a]), the initial rate data gave a straight line corresponding to the expression $-\ln([Co_2Rh_2(CO)_{12}]_t/[Co_2Rh_2(CO)_{12}]_o) = k_1t$ during the first ten minutes of reaction the value of k_1 was 0.07 min^{-1}. In the reaction of $CoRh(CO)_7$ with H_2 (experiment [b]) the initial rate data yielded a straight line according to the expression $\ln([CoRh(CO)_7]_t/[CoRh(CO)_7]_o) = -k_2t$ the value of k_2 was 0.034 min^{-1}. Finally, these two rate constants were used in an expression for the formation of $CoRh(CO)_7$ in experiment [c]: $[CoRh(CO)_7]_t = (2k_1[Co_2Rh_2(CO)_{12}]_o/(k_2 - k_1))(e^{-k_1t} - e^{-k_2t})$. The results of experiment [c], and the predicted data for this experiment calculated from experiments [a] and [b] are presented in Figure 4. The observed concentration of $CoRh(CO)_7$ in experiment [c] agrees with the predicted values within ± 5% over the entire interval studied. This strongly suggests that $Co_2Rh_2(CO)_{12}$ does not react with H_2 to a significant extent under the conditions used.

Our results show that low temperature activation of molecular hydrogen can be achieved by use of $CoRh(CO)_7$ in the presence of carbon monoxide. Although the reaction path is unknown, the formation of an intermediate such as $\{H_2CoRh(CO)_7\}$, and its subsequent fragmentation to give $HCo(CO)_4$ and a very unstable hydridorhodium species such as $\{HRh(CO)_3\}$ [7], which rapidly yields $Rh_4(CO)_{12}$, seems likely.

Experimental

Hexane was distilled from K/Na alloy under nitrogen. $HCo(CO)_4$ [8] $Co_2Rh_2(CO)_{12}$ [5] and $CoRh(CO)_7$ [5] were prepared by published procedures.

IR spectra were taken with a Perkin–Elmer 983 G spectrophotometer connected with a data station 3600 which allowed the subtraction of hexane absorption from the spectra. The following extinction coefficients were used to determine the concentrations of the different species, $HCo(CO)_4$: $\epsilon(2116) = 330$ $dm^3mol^{-1}cm^{-1}$ [9], $Co_2(CO)_8$: $\epsilon(1858) = 1735$ $dm^3mol^{-1}cm^{-1}$ [10], $Rh_4(CO)_{12}$: $\epsilon(1886) = 9030$ $dm^3mol^{-1}cm^{-1}$ [10], $CoRh(CO)_7$: $\epsilon(1956) = 2950$ $dm^3mol^{-1}cm^{-1}$ [11].

All experiments were performed in a stainless steel autoclave connected to a high-pressure IR cell through a recirculating apparatus [11]. $CoRh(CO)_7$ was prepared in situ from $Co_2Rh_2(CO)_{12}$ at 0 °C under 2 bar of CO in n-hexane [5]. The reactions were initiated by charging the autoclave with hydrogen (0.8–8 bar) and were followed by in situ high-pressure infrared spectroscopy.

The new species {X} is very unstable at atmospheric pressures and could not be isolated. The bands at 1918, 1886 and 1869 cm^{-1} are probably due to this species as the ratio between the intensities of the new bands do not change upon its formation and disappearance. There are other bands in the terminal carbonyl region which overlap with bands of $CoRh(CO)_7$, $HCo(CO)_4$, and $Rh_4(CO)_{12}$.

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