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HYDROFORMYLATION OF PROPYLENE WITH HYDROGEN, $Rh_4(CO)_{12}$ AND CARBON MONOXIDE*

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Propylene reacts with H_2 and $Rh_4(CO)_{12}$ at room conditions to yield butyraldehydes and $Rh_6(CO)_{16}$. With higher olefins, isomerization and hydrogenation are observed as side reactions. The rate of butyraldehyde formation is of the first order with respect to $Rh_4(CO)_{12}$ and H_2, and is inhibited by CO, when the latter - if present - is incorporated into the reaction product and partially converts the system into a catalytic one with regard to rhodium. The rate determining step is apparently the reaction of $Rh_4(CO)_{12}$ with H_2 to give mononuclear rhodium carbonyl hydrides and the hydroformylation of propylene is accomplished by these latter species.

The hydroformylation of olefins with rhodium as catalyst [1] is of considerable potential industrial importance because of the high activity and good selectivity of this metal compared to the classical catalyst cobalt. The kinetics and mechanism of hydroformylation in the presence of $Rh_4(CO)_{12}$ has been studied [2], but up

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to the present time many details of the reaction sequence have remained obscure. It is therefore of both theoretical and practical interest to obtain further data regarding the reactions occurring in the rhodium containing hydroformylation reaction mixture.

RESULTS and DISCUSSION

$Rh_4(CO)_{12}$ reacts in toluene under ambient conditions with H_2 and propylene to form normal- and iso-butyraldehyde and $Rh_6(CO)_{16}$ [3]. If the concentration of propylene is high, the reaction is complete at 23°C in about 30 minutes and 90-100 per cent yields of aldehyde can be achieved as expected from Equation (1):

$$3\ Rh_4(CO)_{12} + 4\ H_2 + 4\ C_3H_6 \longrightarrow 4\ C_3H_7CHO + 2\ Rh_6(CO)_{16} \qquad (1)$$

Fig.1. shows the aldehyde formation during a typical experiment.

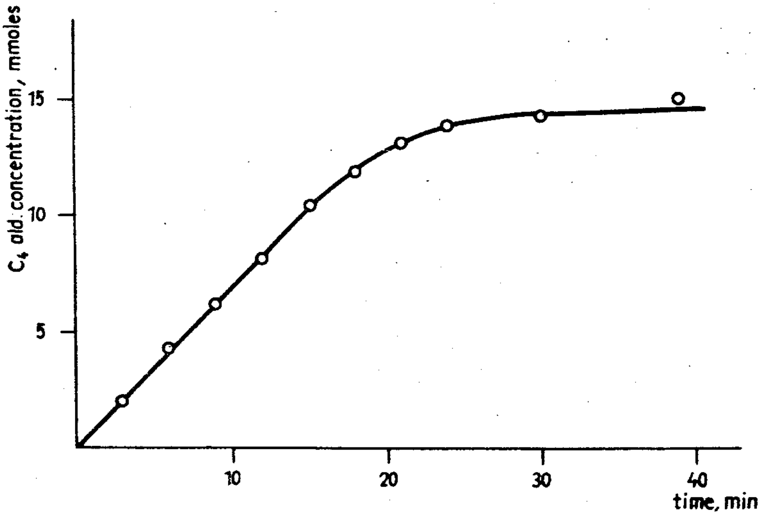

Fig.1. Stoichiometric hydroformylation of propylene in toluene with .0134 moles $Rh_4(CO)_{12}$ at 23°C in the presence of hydrogen; propylene pressure 77.5 mm Hg; hydrogen pressure 388 mm Hg.

This reaction is actually a stoichiometric hydroformylation similar to that described for $Co_2(CO)_8$, H_2 and olefins [4] and thus its study should also provide some information with regard to the catalytic process. Experiments were therefore carried out to determine the kinetics of the aldehyde formation. Only propylene was used as an olefin in these experiments, since preliminary investigations had revealed that higher olefins rapidly isomerize under the conditions used, thus making the evaluation of kinetic data more difficult. In addition, some hydrogenation of the higher olefins was also observed as a side reaction.

The initial rate of butyraldehyde formation was found to be of the first order with respect to p_{H_2} (as shown in Fig.2.), whereas the concentration of $Rh_4(CO)_{12}$ had no effect. The influence of propylene concentration is shown by the results compiled in Table 1. At low concentrations of propylene, the yield of butyralde-

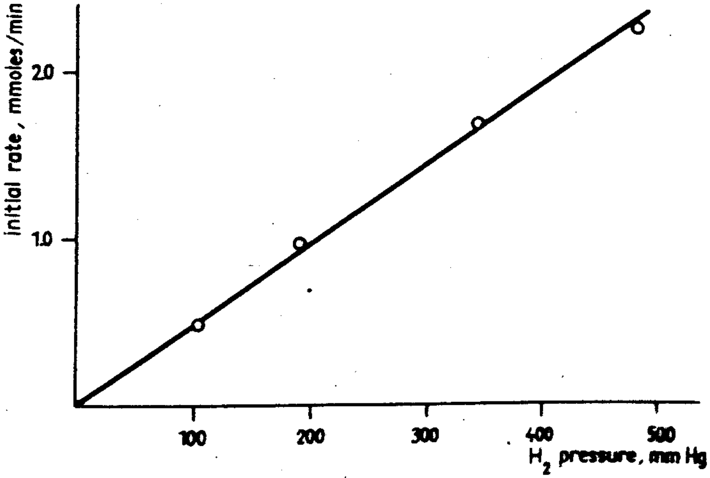

Fig.2. Dependence of initial rate on hydrogen pressure in the absence of carbon monoxide (.0134 moles $Rh_4(CO)_{12}$ in toluene; temp. 23°C; propylene pressure 155 mm Hg).

hyde was appreciably lower than the theoretical 1.33 moles/mole $Rh_4(CO)_{12}$, whereas at high propylene concentrations the rate of butyraldehyde formation was only slightly influenced by $p_{C_3H_6}$.

Table 1. Effect of propylene pressure on hydroformylation (.0134 moles $Rh_4(CO)_{12}$ in toluene; temp. 23°C; hydrogen pressure 232 mm Hg)

propylene pressure (mm Hg)	initial rate of C_3H_7CHO formation (10^{-3} moles/min)	iso/normal aldehyde ratio	aldehyde formed (moles/mole $Rh_4(CO)_{12}$)
22	0.22	2.0-3.0	0.77
51	0.35	2.0-3.0	0.87
78	0.43	1.7-1.9	1.12
142	1.04	1.6-1.7	1.24
245	1.32	1.6-2.0	-

Carbon monoxide exerts a strong inhibiting effect on the initial rate of C_4 aldehyde formation, as shown by Fig.3.; the dependence is approximately described by $(p_{CO})^{-1}$.

It was found that carbon monoxide admixed to the $H_2 + C_3H_6$ gas mixture participates in the reaction and thereby increases the aldehyde yield above 1.33 moles/mole $Rh_4(CO)_{12}$; until the present time, the highest yields achieved were between 3.5-4 moles of C_3H_7CHO/mole $Rh_4(CO)_{12}$. The incorporation of CO into the product obviously decreases its concentration in the reaction mixture and in the gas phase, which leads under appropriate conditions to a characteristic increase of reaction rate within one experiment as shown in Fig.4. By simultaneously monitoring the reaction by IR spectroscopy (for $Rh_4(CO)_{12}$) and gas chromatography (for C_3H_7CHO) it could be shown that as long as the CO concentration is suffi-

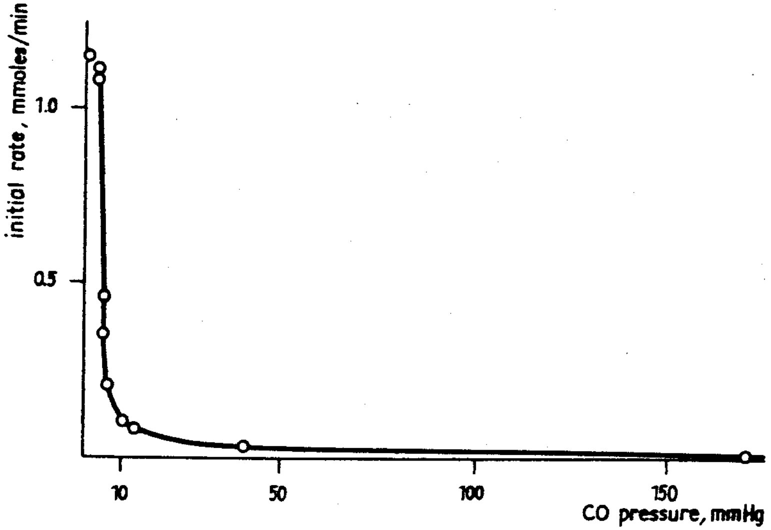

Fig.3. Dependence of initial rate on carbon monoxide pressure (.0134 moles $Rh_4(CO)_{12}$ in toluene; temp. 23°C; hydrogen pressure 232 mm Hg; propylene pressure 155 mm Hg).

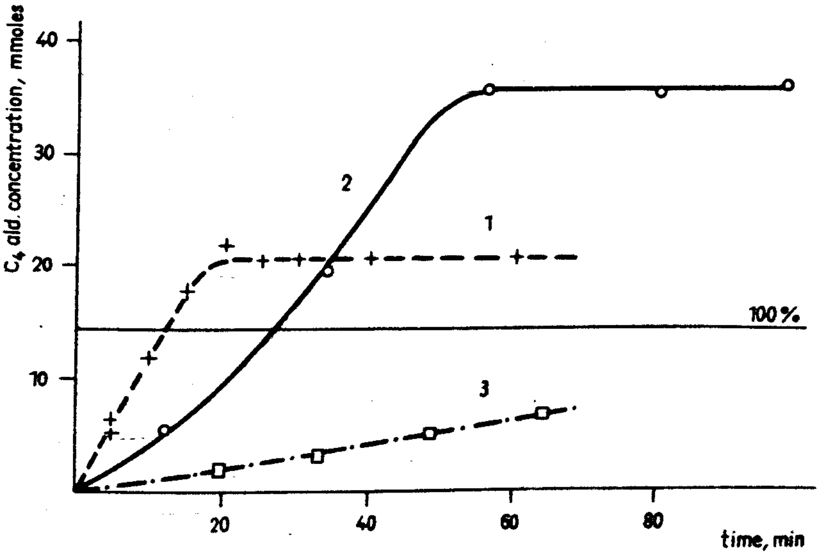

Fig.4. Butyraldehyde concentration vs. time at different carbon monoxide pressure: 1 - CO pressure: 2.5 mm Hg; 2 - CO pressure: 5.1 mm Hg; 3 - CO pressure: 9.8 mm Hg. (.0134 moles $Rh_4(CO)_{12}$ in toluene; temp. 23°C; hydrogen pressure 232 mm Hg; propylene pressure 155 mm Hg).

cient, the decline in the $Rh_4(CO)_{12}$ concentration is moderate (the formation of butyraldehydes is in part due to a "catalytic" effect), while after CO has been consumed, the transformation of $Rh_4(CO)_{12}$ becomes very rapid (Fig.5.).

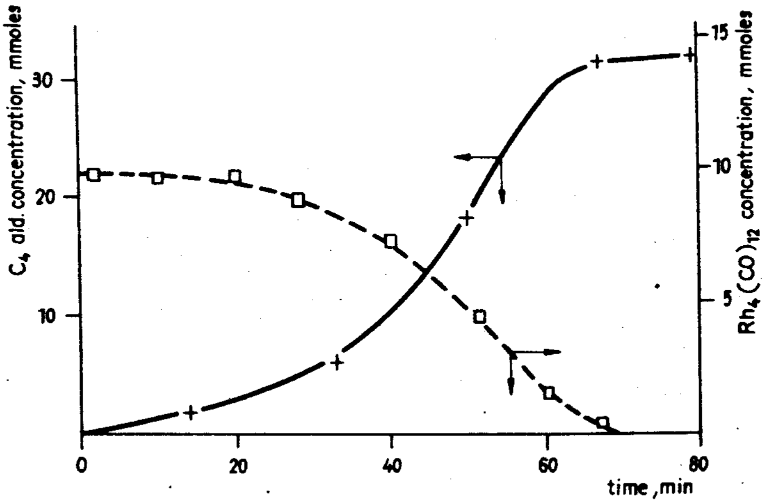

Fig.5. Butyraldehyde and $Rh_4(CO)_{12}$ concentration vs. time (starting $Rh_4(CO)_{12}$ concentration .0098 moles; temp. 23°C; hydrogen pressure 232 mm Hg; propylene pressure 155 mm Hg; carbon monoxide pressure 6 mm Hg).

Under the reaction conditions used, the spontaneous decomposition of $Rh_4(CO)_{12}$ to $Rh_6(CO)_{16}$ and CO cannot be avoided. If no carbon monoxide is added to the gas mixture, the actual p_{CO} is therefore rather ill defined and the kinetic data obtained with the CO-free system can be regarded only as aproximate. For this reason, the kinetics of butyraldehyde formation were also determined at constant low partial pressures of carbon monoxide.

At the actual chosen concentration of carbon monoxide the CO set free by the spontaneous decomposition of $Rh_4(CO)_{12}$ was negligible compared to the quantity of CO added and, at the same time, the rate of butyraldehyde formation was still sufficiently high for practical measurements.

The most remarkable difference was found in the influence of the $Rh_4(CO)_{12}$ concentration. As shown in Fig.6., the initial rate of butyraldehyde formation under constant p_{CO} was of the first order with regard to $Rh_4(CO)_{12}$. The apparent contradiction between the results obtained with and without carbon monoxide can be explained by the compensating effect of CO liberated from $Rh_4(CO)_{12}$, when no carbon monoxide is added to the reaction mixture.

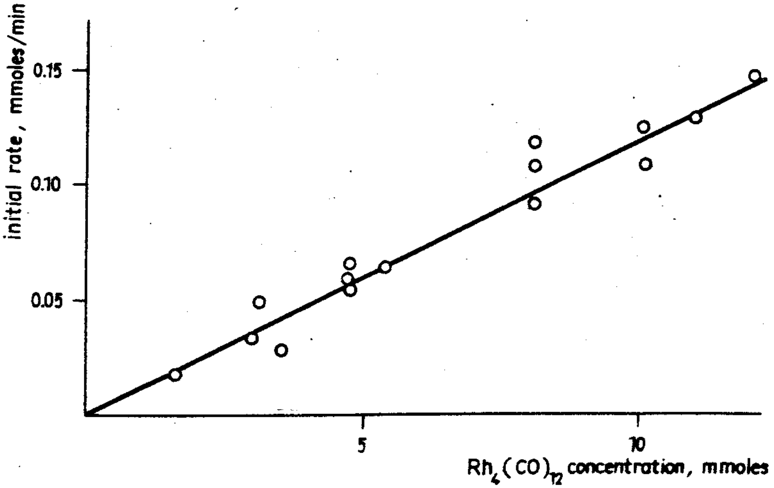

Fig.6. Dependence of initial rate on $Rh_4(CO)_{12}$ concentration (temp. 23°C; hydrogen pressure 232 mm Hg; propylene pressure 155 mm Hg; carbon monoxide pressure 6 mm Hg). The full and open circles refer to two series of experiments.

The results can most appropriately be interpreted by assuming the rupture of the Rh_4 cluster to mononuclear rhodium-carbonyl hydrides as being the rate determining stage. For this process, the following mechanism is suggested:

$$Rh_4(CO)_{12} \rightleftharpoons Rh_4(CO)_{11} + CO \qquad (2)$$

$$Rh_4(CO)_{11} + H_2 \xrightarrow{\text{(rate determining stage)}} \text{mononuclear rhodium-carbonyl hydrides} \qquad (3)$$

The above scheme accords with the observed kinetics

$$\frac{d\ (\text{aldehyde})}{dt} = k\left[Rh_4(CO)_{12}\right]\frac{p_{H_2}}{p_{CO}}$$

This explanation of the experimental results is further supported by those measurements, which show that the rate of $Rh_4(CO)_{12}$ decomposition to $Rh_6(CO)_{16}$ is only very slightly influenced by the absence or presence of propylene (see Table 2.).

Table 2. Effect of propylene on the decomposition of $Rh_4(CO)_{12}$ (starting $Rh_4(CO)_{12}$ concentration .0067 moles in o-xylene; temp. 35°C; hydrogen pressure 310 mm Hg; carbon monoxide pressure 18 mm Hg).

propylene pressure (mm Hg)	percentage of $Rh_4(CO)_{12}$ decomposed in 1 min.
0	0.4
47	0.6
470	1.35

The rate measurements yielded no information on the reaction of the mononuclear rhodium carbonyl hydrides with propylene and the association of the mononuclear fragments to $Rh_6(CO)_{16}$. It is now evident that the actual hydroformylation reaction cycle responsible for aldehyde formation has to be kinetically studied under catalytic conditions (75°C, 100-200 atm.), for this atmospheric system may show how the transformation of $Rh_4(CO)_{12}$ emerges into the catalytically active species ($HRh(CO)_x$). Since this latter process necessarily constitutes the first step in catalytic hydroformylation experiments, the results may be useful for the interpretation of induction periods eventually observed.

EXPERIMENTAL

Materials. All gases were analyzed by GLC. The toluene solvent was purified by distillation, followed by preparative gas-chromatography on a PEG column at 150°C. 0.1 per cent n-Heptane was used as an inner standard.

$Rh_4(CO)_{12}$ was prepared from $Rh_2(CO)_4Cl_2$ at 80°C and 300 atm. CO in the presence of moist $NaHCO_3$ in hexane. The product was separated by chilling the solution to -78°C and purified by recrystallization from hexane.

Apparatus. Experiments were performed in a 50 ml thermostated flask equipped with a magnetic stirrer, silicon rubber tap and a small cup for the $Rh_4(CO)_{12}$, the latter could be overturned from the outside without opening the reaction vessel. Pressure was maintained at 800 mm Hg by a mercury seal.

Reaction of $Rh_4(CO)_{12}$ with Propylene and H_2. $Rh_4(CO)_{12}$ (1 ... 10 mg) was measured into the small cup and the reaction vessel was securated three times with the gas mixture used. 1...2 mℓ solvent was injected by a syringe through the silicon rubber tap and stirred for 20 minutes to ensure saturation. Reaction was started by turning the cup and dropping the $Rh_4(CO)_{12}$ into the solvent where it completely dissolved within less than 1 minute. 10...20 μℓ samples were taken at regular intervals from the reaction mixture with a syringe and stored before analysis at -78°C. The aldehyde formed was determined by GLC (50 m PEG column, 150°C), its quantity was estimated with reference to the n-heptane standard (area of n-heptane to C_4 aldehydes= = 1.60). If the reaction rate was low, the $Rh_4(CO)_{12}$ content of the same samples could be determined by IR spectroscopy, based on the intensity of the 1890 cm^{-1} band.

Acknowledgement

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РЕЗЮМЕ

При обычных условиях пропилен взаимодействует с водородом и $Rh_4(CO)_{12}$ при образовании бутиральдегида и $Rh_6(CO)_{16}$. В случае более высоких олефинов наблюдалисъ в качестве побочных реакций изомеризация и гидрогенизация. Скорость образования бутиральдегида пропорциональна концентрации $Rh_4(CO)_{12}$ или H_2, а обратно пропорциональна концентрации CO. При наличии последней, она встроится в продукт реакции, и система практически превращается в процесс катализированный родием. Определяющим скорость этапом очевидно является реакция $Rh_4(CO)_{12}$ с водородом, когда образуется гидрид карбонила родия с одним ядром, а гидроформилирование пропилена происходит через этот одноядровый комплекс.