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PHOSPHINERHODIUM COMPLEXES AS HOMOGENEOUS CATALYSTS

XI *. DECARBONYLATION OF PRIMARY ALCOHOLS USED AS SOLVENTS UNDER CONDITIONS OF OLEFIN HYDROGENATION; A SIDE REACTION LEADING TO CATALYST DEACTIVATION

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Summary

In the hydrogenation of olefins in alcoholic solvents catalysed by phosphinerhodium complexes a hydrogen transfer reaction from the alcohols to the olefins takes place alongside the main reaction. With primary alcohols the aldehydes formed are decarbonylated and the in situ catalysts formed from $[Rh(diene)Cl]_2$ and phosphines are partially converted into $Rh(CO)(PR_3)_2Cl$ type complexes and thereby deactivated.

Introduction

Hydrogenation of olefins with molecular hydrogen using phosphinerhodium complexes as catalysts is frequently carried out in alcohol solvents, especially ethanol or methanol [1]. However, it has been shown that under more drastic conditions alcohols may function as hydrogen donors in the transfer hydrogenation of olefins with the catalysts described [2—4].

As for as we can ascertain the possibility that in olefin hydrogenation with H_2 the alcohol used as a solvent may also function as a source of hydrogen in a simultaneous transfer hydrogenation process has not previously been investigated, probably because transfer hydrogenation generally occurs at significantly higher temperatures (e.g. above 160°C with $Rh(PPh_3)_3Cl$ as catalyst [2]). This problem may be of practical significance however since from ethanol and methanol aldehydes will be formed, and these in turn will be decarbonylated [5], and the formation of rhodium carbonyl complexes with lead to deactivation of the

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* For part X see ref. 6.

catalyst. We present below results showing that this does happen, and in the case of catalysts prepared from $[Rh(diene)Cl]_2$ and phosphines in situ leads to the formation of catalytically inactive $Rh(CO)(PR_3)_2Cl$ complexes.

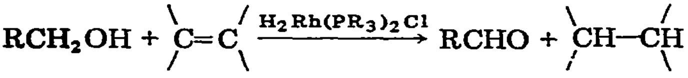
Results and discussion

Several types of olefins were hydrogenated with H_2 in various solvents using as catalysts the rhodium phosphine complexes formed in situ from $[Rh(NBD)Cl]_2$ * and phosphines under hydrogen. Hydrogenations were usually carried on to 50% conversion (as determined from the consumption of H_2), but when the rates were very low the reaction was stopped after 2 h. Following this all volatile compounds were evaporated in vacuo and the $Rh(CO)(PR_3)_2Cl$ content of the residue (usually a dark coloured oil) determined by IR spectroscopy using the characteristic and strong $\nu(CO)$ band of these complexes. The experimental data are compiled in Table 1.

As can be seen from Table 1 in methanol or ethanol a significant part of the rhodium catalyst was transformed into $Rh(CO)(PR_3)_2Cl$ during olefin hydrogenation and this process was enhanced by increasing the temperature (exps. 3—6). Practically no rhodium carbonyl was formed in benzene (exp. 8) or isopropyl alcohol (exp. 7) as solvents or in the absence of an olefinic substrate (exp. 1 and 2). A saturated ketone such as ethyl methyl ketone, which is also hydrogenated under such conditions, did not promote the decarbonylation reaction (exp. 18 and 19). Obviously not only the alcohols, but also the olefins were necessary for carbonyl-complex formation.

This fact was even more clearly brought out by the experiments shown in Fig. 1. The conversion of the olefin (in this case styrene) and the formation of the rhodium carbonyl ran reasonably parallel. After all the olefin had been hydrogenated, no further carbonyl complex was formed. Correspondingly, when the amount of olefin to be hydrogenated was increased, $Rh(CO)(PR_3)_2Cl$ formation was also enhanced; thus in the hydrogenation of 270 moles of 2-methyl-1-pentene per mole rhodium, 60% of the latter was converted into the carbonyl complex. At the same time a rather strong fall off in the rate of hydrogenation was observed.

These facts strongly suggest that under the conditions used rhodium complexes such as $H_2Rh(PR_3)_2Cl$ catalyze not only the hydrogenation of olefins by molecular hydrogen but also the transfer of hydrogen from the alcohol to the olefin (eq. 1) the aldehyde so formed then being decarbonylated by the complex (eq. 2):



$$RCH_2OH + \rangle C{=}C\langle \xrightarrow{H_2Rh(PR_3)_2Cl} RCHO + \rangle CH{-}CH\langle \qquad (1)$$

$$RCHO + H_2Rh(PR_3)_2Cl \rightarrow Rh(CO)(PR_3)_2Cl + RH + H_2 \qquad (2)$$

$R = H, CH_3$

These proposals were confirmed by the following observations.

a) When isopropyl alcohol was used as solvent (exp. 7), 0.33 mmol acetone

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* NBD = norbornadiene.

TABLE 1

HYDROGENATION OF DIFFERENT OLEFINS. [a] FORMATION OF $Rh(CO)(PR_3)_2Cl$ COMPLEXES

No	Olefin	Phosphine	Solvent	$Rh(CO)(PR_3)_2Cl$ [b]
1	—	PPh_2Et	MeOH	not detectable [d]
2	—	PPh_2Et	EtOH	not detectable [d]
3	Styrene	PPh_2Et	MeOH	13
4	Styrene	PPh_2Et	EtOH	55
5	Styrene	PPh_2Et	MeOH	3 [c]
6	Styrene	PPh_2Et	EtOH	25 [c]
7	Styrene	PPh_2Et	i-PrOH	not detectable
8	Styrene	PPh_2Et	Benzene	not detectable
9	Styrene	PPh_3	MeOH	10
10	Styrene	$Pn\text{-}Bu_3$	MeOH	16
11	2-Methyl-1-pentene	PPh_2Et	MeOH	10
12	2-Methyl-1-pentene	PPh_2Et	EtOH	25
13	Methyl acrylate	PPh_2Et	MeOH	22
14	Methyl acrylate	PPh_2Et	EtOH	16
15	Mesityl oxide	PPh_2Et	MeOH	3
16	Mesityl oxide	PPh_2Et	EtOH	14 [d]
17	Ethyl cinnamate	PPh_2Et	MeOH	27
18	Ethyl methyl ketone	PPh_2Et	MeOH	not detectable [d]
19	Ethyl methyl ketone	PPh_2Et	EtOH	not detectable [d]

[a] 0.025 mmol $[Rh(NBD)Cl]_2$, 0.15 mmol phosphine, 5 mmol substrate, 12 ml solvent, 1 bar H_2, 50°C. [b] Fraction of rhodium transformed into $Rh(CO)(PR_3)_2Cl$, during 50% conversion of olefin (hydrogenation of 2.5 mmol substrate). [c] 30°C. [d] Reaction time 2 h.

was found by GLC (PEG, 50 m glass capillary column, 100°C) in the product mixture after the hydrogenation of 2.5 mmol styrene with molecular hydrogen (i.e. an additional 0.33 mmol of styrene was hydrogenated by a hydrogen transfer mechanism);

b) Upon adding 0.6 mol acetaldehyde per mol rhodium to an ethanol solution of $[Rh(NBD)Cl]_2$ and PPh_2Et (P/Rh = 3/1) and after treating this mixture

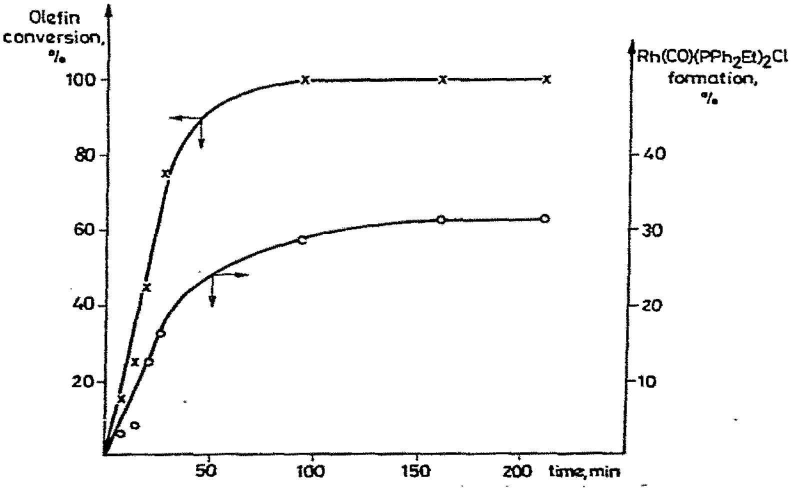

Fig. 1. Formation of $Rh(CO)(PPh_2Et)_2Cl$ during the hydrogenation of styrene in methanol solution. 0.025 mmol $[Rh(NBD)Cl]_2$, 0.15 mmol PPh_2Et, 5 mmol styrene, 12 ml methanol, 50°C and 1 bar H_2.

at 50° C with H_2 for 2 h, 11% of the rhodium was transformed to $Rh(CO)(PPh_2Et)_2Cl$ (cf. exp. 2 in which no carbonyl complex was formed under such conditions in the absence of acetaldehyde);

c) Methane formed during the hydrogenation of styrene in ethanol as solvent was detected in the gas phase by GLC (squalane, 100 m glass capillary column, 100° C).

Our results indicate the need for caution in using primary alcohols as solvents for olefin hydrogenations with rhodium phosphine catalysts. Clearly such solvents cannot be totally ruled out because of their many favourable properties, but the extent of this type of catalyst deactivation should be checked.

Experimental

General procedure

11.6 mg (0.025 mmol) $[Rh(NBD)Cl]_2$ and 31.1 mg (31.1 μl, 0.15 mmol) PPh_2Et were dissolved in 12 ml methanol or ethanol and prehydrogenated at 50° C for 30 min. in a thermostatted flask connected to a thermostatted gas burette and equipped with a magnetic stirrer and a silicone rubber cap. The olefin (5 mmol) was then added with a syringe and the reaction was monitored by measuring the hydrogen consumption. After 50% of the olefin had been hydrogenated, the product was evaporated to dryness in vacuo, and the residue was dissolved in CH_2Cl_2 and its IR spectrum determined in the 2200—1800 cm^{-1} region.

The quantity of $Rh(CO)(PPh_2Et)_2Cl$ formed was calculated by comparing the intensity of the $\nu(CO)$ band at 1968 cm^{-1} (corrected for absorptions due to components of the catalyst) with that of solutions of the same complex with known concentrations. The $Rh(CO)(PPh_2Et)_2Cl$ necessary for this calibration was prepared by hydrogenating $[Rh(NBD)Cl]_2$ in methanol in the presence of PPh_2Et (P/Rh = 3/1) and treating the product with CO. Its purity was checked by IR spectroscopy and elemental analysis.

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