

## THE ACTIVITY OF HOMOGENEOUS AND HETEROGENIZED Rh(I) COMPLEXES IN HYDROGENATION OF ALKENES\*

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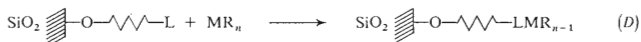
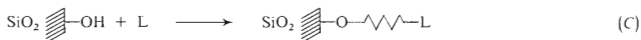
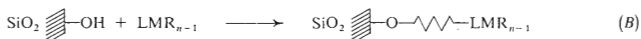
Kinetics of liquid phase hydrogenation of alkenes catalysed by homogeneous Rh(I) complexes prepared *in situ* from di- $\mu, \mu'$ -chloro-bis(di(cyclooctene)rhodium) and 3-(triethoxysilyl)propyldiphenylphosphine and by heterogenised analogues anchored to silica have been studied. The reaction was found to be first order in hydrogen, alkene and catalyst. Compared to the soluble complexes, the supported catalysts turned out to be substantially more stable. At 0.3–0.6% Rh concentrations on the support, the activity of the catalysts was not affected by pore size within 4–10 nm region. The supported catalysts prepared by functionalization of the support followed by formation of the Rh complex were more active than their homogeneous analogues.

In last ten years much effort has been devoted to the study of the so called heterogenised catalysts, *i.e.* to the use of transition metal complexes coordinately bound to organic or inorganic supports as catalysts. Although many promising results have been obtained in this field (for review see refs<sup>1,2</sup>) and in some cases heterogenised catalysts showed higher activity compared to their soluble analogues<sup>3–5</sup>, this is not, however, general phenomenon<sup>6–8</sup>. As a rule, fixation of coordination compounds to supports brings the problems and limitations of heterogeneous catalysis which are not still well clarified<sup>2</sup>.

The aim of the present work was to contribute to the knowledge of the factors connected with heterogenization of homogeneous catalysts, especially the role of porosity of the support, degree of covering of its surface, the ligand to metal ratio and the way of fixation of the complex. For this purpose we chose silica as a support. This allowed to vary these factors over wide range. The properties of catalysts were examined by kinetic study of hydrogenation of alkenes. The hydrogenation was carried out under constant hydrogen pressure, which suitably simplified kinetics of the reaction. With regard to the fact that recently prepared ligand (3-triethoxysilylpropyldiphenylphosphine) was used, the effect of which on catalytic properties of rhodium compounds has not yet been reported, it was necessary to examine also the behaviour of the soluble complexes containing this ligand, particularly to determine the order of the reaction with respect to individual components.

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The use of silica and the phosphine substituted with triethoxysilyl group allowed further to compare the catalytic activity of supported rhodium complexes prepared by two procedures: *a*) by fixation of the soluble complex prepared in solution (equations (A) and (B)) and *b*) by functionalization of the support (equation (C)) followed by formation of the complex *via* interaction of the appropriate precursor with the so modified support (equation (D)).



## EXPERIMENTAL

**Chemicals.** Rhodium trichloride (Safina, Vestec), alkenes, diphenylphosphine (Fluka, Buchs A. G.) were used without further purification. 3-Chloropropyltrichlorosilane<sup>10</sup> and -triethoxysilane<sup>10</sup>, (3-triethoxysilyl)propyl-diphenylphosphine<sup>9</sup> and di- $\mu$ , $\mu'$ -chloro-bis(dicyclooctenerhodium)<sup>11</sup> were prepared by reported procedures as indicated.

**Supports.** Two silicas supplied by Merck were used, both having 0.063—0.200 mm particles: Kieselgel 40 (4 nm mean pore size, 632 m<sup>2</sup>/g specific surface) and Kieselgel 100 (10 nm mean pore size, 365 m<sup>2</sup>/g specific surface).

**Soluble catalysts** were prepared *in situ* from  $[\{\text{RhCl}(\text{C}_8\text{H}_{14})_2\}_2]$  and (3-triethoxysilyl)propyl-diphenylphosphine in toluene. Because of low solubility of the complex formed, only very dilute solutions could be prepared. Two series of homogeneous catalysts were used in which Rh/P molar ratio equaled to 1 : 3 and 1 : 2 (Table I).

**Heterogenised catalysts.** Procedure *A* (equations (A) and (B)). Approximately twofold volume of dry toluene was added to the known amount of dried silica (200°C/1.4 kPa, 5 h) and then a solution of homogeneous catalyst freshly prepared *in situ* as described in the preceding paragraph was dropwise added with stirring. After refluxing the mixture for one hour, *c.* half the volume of toluene was removed by distillation, the catalyst was filtered off, washed twice with toluene (*c.* twofold volume) and washing was eventually repeated until the extract was colourless. Then the catalyst was dried under high vacuum for two hours.

Procedure *B* (equations (C) and (D)). The dried silica was allowed to react with (3-triethoxysilyl)propyl-diphenylphosphine in toluene. After refluxing the mixture for one hour, the rhodium-cyclooctene complex dissolved in toluene was added, the mixture was refluxed for another hour. Further procedure was the same as in the preceding case (for ratios of components and Rh content see Table I).

*Hydrogenation* was carried out under constant hydrogen pressure using the apparatus reported earlier<sup>12</sup>. Relative rate constants for hydrogenation of isomeric heptenes were determined from competition hydrogenations using heptene-1-methylstyrene mixture, those for cyclohexene using of 1-heptene-cyclohexene mixture. Heptane to 2-phenylpropane ratio was determined chromatographically on Chrom 3 apparatus equipped with 50 m capillary column (0.2 mm *i.d.*) filled with tricresyl phosphate at 120°C (oven temperature). Cyclohexane to heptane ratio was determined analogously, using Chrom 4 instrument equipped with 3.6 m column (3 mm *i.d.*) packed with 18% ethylene glycol-bis(propionitrile) ether on Chromaton N-AW (0.20–0.25) at 25°C (oven temperature). In both cases hydrogen was used as a carrier gas. Synthesis of complexes and kinetic measurements were carried out under anaerobic conditions<sup>13</sup>.

## RESULTS AND DISCUSSION

After having found the conditions under which the effect of macrokinetic effects was excluded, we examined the order of the reaction in individual components. It was found by van Hoff differential method<sup>14</sup> that for soluble catalyst A (Rh/P = 1 : 2) and 50–130 kPa hydrogen pressures at 44°C the order in hydrogen is 1.05 and for complex B (Rh/P = 1 : 3) it is 0.94. This finding agrees with the results of some related studies in which hydrogenation of alkenes catalysed by Wilkinson complex  $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$  was reported to be approximately first-order in hydro-

TABLE I  
Catalysts Used

Catalyst	Support <sup>a</sup> (g)	(Ph) <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> mmol	Rh <sub>2</sub> Cl <sub>2</sub> (C <sub>8</sub> H <sub>14</sub> ) <sub>4</sub> mmol	Mol. ratio Rh : P	Rh content %
A	—	20.54 <sup>b</sup>	5.13	1 : 2	—
B	—	37.80 <sup>c</sup>	6.30	1 : 3	—
C	100 (20.1)	1.21	0.30	1 : 2	0.32
D	40 (20.1)	1.21	0.30	1 : 2	0.33
E	100 (10.1)	3.94	0.98	1 : 2	0.79
F	40 (10.1)	3.94	0.98	1 : 2	1.11
G	100 (19.3)	2.42	0.40	1 : 3	0.50
H	100 (11.2)	3.86	0.64	1 : 3	0.84
I	100 (12.1)	1.24	0.31	1 : 2	0.58
J <sup>d</sup>	100 (12.3)	1.37	0.34	1 : 2	0.61
K	100 (7)	1.00	0.12	1 : 4	0.37

<sup>a</sup> 100 = Kieselgel 100; 40 = Kieselgel 40; <sup>b</sup> in 306 ml of toluene; <sup>c</sup> in 470 ml of toluene; <sup>d</sup> prepared according to procedure B (see Experimental).

gen<sup>15,16</sup>. Further kinetic measurements were carried out under constant hydrogen pressure (pseudo-zeroth order in hydrogen).

The order of hydrogenation with respect to catalyst determined by the differential method from initial reaction rates is presented in Table II. Although reproducibility of the results is decreased by the employed graphical derivation of the conversion curve, it remains on the level which is usually achieved in kinetic measurements of homogeneously catalysed reactions<sup>17</sup>. With regard to this, one can presume that the reaction is first-order in the catalyst, in accordance with data reported<sup>15</sup> for hydrogenation catalysed by Wilkinson complex.

Since there are controversial data in literature<sup>17,18</sup> concerning the effect of admixtures of oxygen on the course of homogeneously catalysed hydrogenation we paid attention also to this effect. Fig. 1 shows that the addition of oxygen (simultaneously with alkene) in the amount of approximately 0.7% of the volume of the gas phase in the reactor does not affect the initial reaction rate but it gradually decreases the activity of the catalyst during the reaction until its complete deactivation. When the catalyst solution is exposed to oxygen prior to alkene addition, the reaction essentially did not take place. Therefore, it is reasonable to assume that the activity decrease is caused by deactivation of the initially formed rhodium-hydride complex.

In determining the order of hydrogenation in alkene, the first order in the substrate was postulated. This assumption was verified for all the catalysts by a good agreement of obtained data with the integral form of the first order equation (Fig. 2), again in harmony with the results for related rhodium-phosphine complexes<sup>15,19,20</sup>.

TABLE II

## Hydrogenation of 1-Heptene — the Order of the Reaction in Catalyst

Reaction temperature 65.5°C, hydrogen overpressure 14.93 kPa, 2 ml of 1-heptene, 0.01–0.1 mmol Rh(I), 18 ml of toluene, determined from three to five measurements.

Catalyst	Reaction order	Catalyst	Reaction order
A <sup>a</sup>	1.09	B	1.11
C	1.12	G	0.99
D	1.13	H	1.00
E	1.24	I	0.89
F	0.90	J	1.27

<sup>a</sup> Reaction temperature 33°C.

Hydrogenation of alkenes in the presence of soluble and heterogenised rhodium complexes containing (3-triethoxysilylpropyl)diphenylphosphine is thus first order in hydrogen, catalyst and alkene, analogously to the behaviour of rhodium complexes with triphenylphosphine as ligand<sup>17,19</sup>. This indicates that hydrogenation on catalysts of both types proceeds by identical reaction mechanism.

Since one of the factors influencing the activity of supported catalysts may be also the degree of covering of the support surface by the complex, the attention was paid also to this question. It was found that maximal capacity attained with the procedure used for fixation is 0.8% Rh for silica with 10 nm mean pore size and 1.1% Rh for silica with smaller pores (4 nm). These values are not proportional to surfaces of these supports (365 and 632 m<sup>2</sup>/g) and show that the support with smaller pores contains also micropores into which the bulky complex cannot penetrate. At such a maximal degree of covering it is not possible to exclude that some complexes are fixed to the support only by physical forces. For this reason most of the catalysts used in kinetic study had 0.3–0.6% Rh content. In these cases anchoring of the catalyst proceeds readily. As in all the extracts after washing the supported catalysts the metal was essentially absent, these procedures are also more economic.

The use of these procedures led also to good agreement between rhodium concentrations calculated from the weighed amounts and determined analytically. Thus for example catalysts C and D contained 0.32 and 0.33% Rh, respectively, according

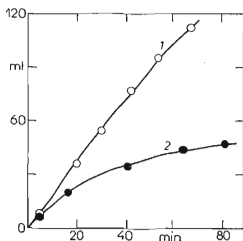


FIG. 1

The Effect of Oxygen on the Rate of 1-Heptene Hydrogenation

1-Heptene (2 ml), catalyst C(Rh(I) conc. 0.003M), volume 20 ml, hydrogen overpressure 14.93 kPa. 1 in the absence of oxygen, 2 0.7% O<sub>2</sub> added simultaneously with 1-heptene. volume of consumed hydrogen (ml), reaction time (min).

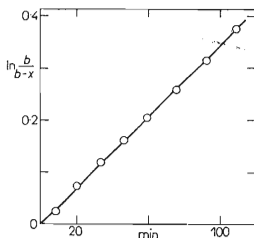


FIG. 2

$\ln b/(b-x)$  vs  $t$  Plot for Hydrogenation of 1-Heptene (2 ml)

Catalyst E (Rh conc. 0.003M), volume 20 ml, hydrogen overpressure 15 kPa.  $b$  is the initial 1-heptene concentration,  $b-x$  denotes the heptene concentration at time  $t$ .

to analysis, while 0.30 and 0.31% Rh was obtained by calculation. The lower rhodium concentrations on support (c. 0.1%) were found to be unsuitable.

In Table III are given rate constants for hydrogenation of 1-heptene for the catalysts used. From comparison of the activities of catalysts A and B it becomes obvious that in homogeneous phase the increasing excess of ligand leads to the decrease in the catalyst activity. The same trend was observed also for the catalysts fixed to the same support and the same degree of surface covering (I and G, C and K, E and H). This finding is in accordance with the observation that the excess of ligand prevents formation of free coordination site<sup>17</sup>. With fourfold excess of the ligand the catalyst is essentially inactive (catalyst K).

Comparison of the activities of homogeneous and heterogenised catalysts from the point of view of the effect of pore size of the support is also of interest. At the same, but not maximal, rhodium concentration on the support no decrease in the activity of the catalyst has been found on changing pore size from 10 nm to 4 nm (compare catalysts C and D, C<sup>c</sup> and D<sup>c</sup>). Fixation of complexes on the surface of the support with small pores does not therefore lead to such narrowing the pores which would prevent penetration of reaction components to active sites. A different situation

TABLE III

Rate Constants for Hydrogenation of 1-Heptene Catalysed by Rhodium Complexes  
For conditions see Table II.

Catalyst	Support <sup>a</sup>	Rh content %	Molar ratio Rh : P	$k$ l mol <sup>-1</sup> min <sup>-1</sup>
A	homogeneous		1 : 2	2.41
A <sup>b</sup>	homogeneous		1 : 2	1.33
B	homogeneous		1 : 3	1.07
C <sup>b</sup>	10	0.32	1 : 2	0.14
D <sup>b</sup>	4	0.33	1 : 2	0.16
C	10	0.32	1 : 2	1.52
D	4	0.33	1 : 2	1.47
E <sup>c</sup>	10	0.79	1 : 2	1.41
F <sup>c</sup>	4	1.11	1 : 2	0.97
G	10	0.50	1 : 3	0.80
H <sup>c</sup>	10	0.84	1 : 3	0.89
I	10	0.58	1 : 2	1.69
J	10	0.61	1 : 2	3.12
K	10	0.37	1 : 4	<0.1

<sup>a</sup> The value denotes mean pore size (in nm) for silica used; <sup>b</sup> reaction temperature 33°C; <sup>c</sup> maximal rhodium concentration achieved.

has been, however, encountered on using the catalysts which were intentionally prepared so that maximal concentration of rhodium complex on support be attained. While in the case of the support with large pores (10 nm) the decrease in the catalyst activity is hardly detectable (*cf.* complexes C and E), it is distinct for the support with small pores (complexes D and F, E and F). In the latter case two phenomena play likely a role; the accessibility of active sites is reduced by the presence of a part of rhodium complex in micropores and at the same time the penetration into small pores is made so difficult that microkinetic effects become significant. Heterogenised catalysts C–I are less efficient than their homogeneous analogues. On the other side, they are of advantage due to their very good stability. A solution of homogeneous catalyst had to be tested the same day (otherwise it lost its activity), while heterogenised catalysts could be stored at least for two months without appreciable change in their activity. Likely due to dynamic ligand exchange<sup>6</sup>, during hydrogenations catalysed by heterogenised catalysts the extraction of a small amount of rhodium from the support surface to solution could not be fully prevented. The amount of the rhodium complex present in solution increased with increasing temperature and concentration of the metal on support.

In order to make heterogenised catalysts more advantageous from the point of view of their applicability, we looked for the possibility to increase their catalytic activity. It was already assumed<sup>4,21,22</sup> that the lower activity of heterogenised catalysts is caused by dimerisation and conglomeration of active sites. This is likely the case with the supported complexes prepared according to equations (A) and (B). In contrast to this, formation of such conglomerates is strongly suppressed when the

TABLE IV

## Relative Rate Constants for Hydrogenation of Alkenes

Homogeneous catalyst A (Rh : P = 1 : 2), heterogenised catalyst I (Rg : P = 1 : 2; 0.58% Rh), for conditions see Table II,  $k_{rel}$  for  $\alpha$ -methylstyrene = 0.93.

Olefin	$k_{rel}$ for the catalyst	
	homogeneous	heterogenised
1-Heptene	1.00	1.30
<i>cis</i> -2-Heptene	0.70	0.71
<i>trans</i> -2-Heptene	0.17	0.42
<i>trans</i> -3-Heptene	0.13	0.24
Cyclohexene	0.58	0.39
$\alpha$ -Methylstyrene	0.93	0.93 <sup>a</sup>

<sup>a</sup>  $k_{rel} = 0.39$  for the catalyst G (Rh : P = 1 : 3; 0.50% Rh).

support surface is first modified by the ligand and then the supported complex is formed by ligand exchange (equations (C) and (D)). By this way we prepared catalyst J which was twice as active as the catalyst obtained by the procedure represented schematically by equations (A) and (B) and also nearly 1.5 times more active than the homogeneous analogue (catalyst (A)).

In addition to examination of the activities of individual catalysts we examined also the effect of the above mentioned factors on their selectivities, which were determined by means of competition reactions (Table IV). The accuracy of the values obtained is documented by the fact that the relative rate constant  $k_{rel}$  for cyclohexene with respect to 1-heptene calculated from competition experiment (0.46) agreed well with the values determined from the rate constants for both alkenes ( $k = 2.41 \text{ l mol}^{-1} \text{ min}^{-1}$  for 1-heptene and  $1.25 \text{ l mol}^{-1} \text{ min}^{-1}$  for cyclohexene;  $k_{rel} = 0.52$ ) determined by integral method. The sequence of relative rate constants of isomeric heptenes for their hydrogenation in homogeneous phase is in harmony with data reported for hydrogenation of alkenes<sup>20,23,24</sup> catalysed by Wilkinson catalyst: 1-alkene > *cis*-2-alkene  $\gg$  *trans*-2-alkene > 3-alkene, in accordance with the presumed *cis*-addition of hydrogen. The same trend was found also for heterogenised catalysts, small variations in the value being probably due to the changed accessibility of active sites in the vicinity of surface.

It can thus be concluded that hydrogenation catalysed by rhodium complexes containing (3-triethoxysilyl)propyldiphenylphosphine proceeds via the same mechanism and kinetics as hydrogenation catalysed by Wilkinson catalyst. Their anchoring to inorganic supports yields catalysts which are more stable and in some cases also more active compared to homogeneous analogues. The texture of the support and the concentration of rhodium complexes on support surface affect the activity and selectivity of these catalysts only to a small extent.

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