# HYDROGENATION ACTIVITY OF HOMOGENEOUS AND HETEROGENIZED CYCLOPENTADIENYL TITANIUM COMPLEXES

Martin ČAPKA and Alena REISSOVÁ

*Institute of Chemical Process Fundamentals,*
*Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchdol*

Hydrogenation of alkenes and cycloalkenes catalyzed by a reduced bis(cyclopentadienyl)dichlorotitanium(IV) complex and by its immobilized analogue coordinately bound to silica has been studied. With both catalytic systems, the rate constants and reaction orders to individual components were determined in 10—60°C temperature region and at a pressure of 0·1 MPa and mechanism of the reaction has been proposed. Kinetic measurements and EPR spectra proved that the immobilized catalysts remain firmly bound to the support during whole catalytic cycle, which made their reuse possible.

Immobilized hydrogenation catalysts based on transition metal complexes still attract special attention[1,2]. The main interest is centered on phosphine complexes of platinum metals. These, however, are rather expensive and are thus applied to the synthesis of costly, especially pharmaceutical products[3]. On the other hand, it is known that cheap, reduced cyclopentadienyl titanium complexes are also very efficient hydrogenation catalysts[4]. Nevertheless, there are only few reports on the successful application of their immobilized analogues (cf. refs[5-8]). The activity of such catalysts was as a rule lower than that of heterogenized rhodium catalysts and anchored titanium complexes lost their activity on reuse, which could be caused by the fact that the anchored complex is not strictly titanocene analogue.

However, in our previous work[9] we proved that with the use of the cyclopentadienyl-functionalized silica a stepwise process leads to the formation of titanium complexes, the immobilized form of which coresponds to the titanocene monomer. Therefore, in the present study we concentrated on comparison of the hydrogenation activity of the reduced homogeneous and immobilized bis(cyclopentadienyl)titanium-(IV) complex and on the factors which affect its activity, stability and reusability. The aim of the study was to synthesize titanium catalysts which in activity would be comparable to rhodium-phosphine complexes.

## EXPERIMENTAL

The catalysts used were the reduced bis($h^5$-cyclopentadiene)dichlorotitanium(IV) complexes, the synthesis of which was reported by us earlier[9]; the substrates and solvents were commerical products (Fluka AG, Buchs). They were dried before use and thoroughly freed of oxygen traces[10]. The purity of the starting compounds and the composition of products was followed by gas chromatography (Chrom 5 instrument produced by Laboratorní přístroje Prague). The course of hydrogenations was followed kinetically with the use of the apparatus working under strictly inert conditions and at constant hydrogen pressure, provided with electric recording of hydrogen consumption[11]. EPR spectra were measured at room temperature, using ERS-200 spectrometer. Measurements were performed with a special arrangement, which consisted in the cell connected to the hydrogenation vessel such that after replacement of hydrogen by argon, the vessel containing reaction mixture and the cell could be separately sealed off. This made it possible to record separately the EPR spectra of the liquid and solid phase.

## RESULTS AND DISCUSSION

### Homogeneous Hydrogenation

In order to understand the behaviour of immobilized titanium(IV) catalysts, mechanism of the reduced bis(cyclopentadienyl)dichlorotitanium(IV) complexes should be examined first. We have found that the reduced $Cp_2TiCl_2$ ($Cp = C_5H_5$) catalyses hydrogenation of 1-alkenes under atmospheric pressure and mildly increased temperature ($40-60°C$). The catalytic active form proper was prepared in situ in the reaction vessel by adding butyllithium to toluene solution of $Cp_2TiCl_2$. This led to characteristic darkening of the solution and this colour remained unchanged both during hydrogenation and after its completion. Discolouration to light yellow solution proceeded only in the presence of air. On adding the reactants in the order $Cp_2TiCl_2$, butyllithium, and alkene, the initial reaction rate $r^0$ decreases in dependence on time after which alkene was added (after 5 min interval the initial rate decreased to 89 per cent and after 10 min interval to 84 per cent of the original value). The decrease of initial reaction rate in the absence of alkene can be ascribed to dimerization of the active species[12] and this problem will be discussed later. For the above finding, further experiments were made with the following sequence of the reactants: $Cp_2TiCl_2$, alkene, butyllithium. When studying the dependence of the initial reaction rate on the $Cp_2TiCl_2$ to $C_4H_9Li$ molar ratio we have found that the initial rate increases up to the ratio of 1 : 10 and at the higher excess of the reducing agent it again decreases. Therefore, further experiments were made with the 1 : 10 molar ratio.

Gas chromatographic analysis of partly hydrogenated reaction mixture showed that 1-octene is not isomerized during hydrogenation, since even traces of octenes with internal double bond have not been detected.
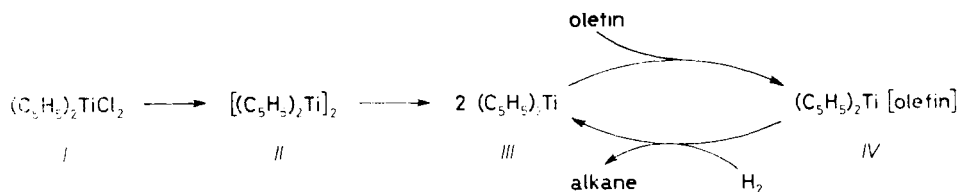
We have also examined the effect of alkene structure on hydrogenation rate $\left(c_{alkene} = 0·291 \text{ mol } l^{-1}, c_{cat} = 0·715 . 10^{-3} \text{ mol } l^{-1}, p(H_2) = 96·1 \text{ kPa}, t = 60°C\right)$.

The following initial rates $(r^0 . 10^3$ in mol $1^{-1} s^{-1})$ were found: 1-octene 14·1, 1-heptene 17·3, cyclodecene 6·0, cyclooctene 14·0, cycloheptene 8·7, cyclohexene 10·0, cyclopentene 10·7. Heptenes with internal double bond, 1-heptyne, 4,4-dimethyl-1-pentene and 3,3-dimethyl-1-butene were not hydrogenated. The above initial rates are substantially higher compared to data reported by Brubaker and Grubbs[5] which in the latter case could be caused by improper charging sequence of the reactants. Coordination of alkene is obviously affected by steric effects. This is indicated by the fact that the alkenes with enriched electron density of C=C bond are not hydrogenated if they contain bulky tert. butyl group, e.g. 3,3-dimethyl-1-butene and 4,4-dimethyl-1-pentene. In this connection somewhat surprising is the relatively high reactivity of cycloalkenes which in electron density of the C=C bond and in steric demands are similar to internal alkenes. These are, however, hydrogenated at the same rate as 1-alkenes. On comparing the rate of hydrogenation of cycloalkenes on their ring size it is seen that of the trend of decreasing reactivity with increasing ring size, cyclooctene represents a significant exception. The extraordinarily high reactivity of cyclooctene was, however, already reported in the case of hydrogenations catalysed both by heterogeneous catalysts[13,14] and by the homogeneous ruthenium complex[15] $RuCl_2[P(C_6H_5)_3]_3$.

Dependence of the initial reaction rate of hydrogenation of 1-octene catalysed by the reduced $Cp_2TiCl_2$ $(c_{cat} = 4·8 . 10^{-4}$ mol $1^{-1}$, $c_{alkene} = 0·291$ mol $1^{-1}$, $p(H_2) = 96·1$ kPa) on temperature is demonstrated by the following data: for reaction temperatures 10, 20, 30, 40, 50, and 60°C $r^0 . 10^3$ $(mol 1^{-1} s^{-1})$ were successively 2·6, 3·5, 4·5, 6·6, 8·8, and 11·8. Based on these data the activation enthalpy $\Delta H^{\neq}$ equaled to 23·76 kJ mol$^{-1}$ and activation entropy $\Delta S^{\neq} = -127·8$ J mol$^{-1}$ K$^{-1}$.

We have also determined the reaction order in the individual reaction components. It was found that the reaction is zero order to hydrogen, first order to alkene and, surprisingly, half order to the catalyst. These reaction orders cannot be accounted for by any of the mechanisms proposed so far for this hydrogenation.

We believe that the above data can be explained by the mechanism depicted in Scheme 1. We are aware of the fact that this mechanism is simplified and that be-



$$(C_5H_5)_2TiCl_2 \longrightarrow [(C_5H_5)_2Ti]_2 \longrightarrow 2 (C_5H_5)_2Ti \quad (C_5H_5)_2Ti [olefin]$$

$$I \qquad\qquad II \qquad\qquad III \qquad\qquad IV$$

olefin, alkane, $H_2$

SCHEME 1

tween individual steps there exists series of interstages. Of course, eventually also another mechanism would in principle be compatible with the above findings.
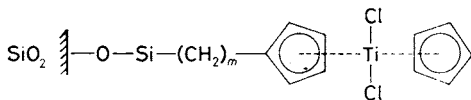
To describe the mechanism now proposed, we suppose that by tenfold excess of butyllithium, the starting titanium(IV) complex (*I*) is completely reduced to a dimer complex of low valent titanium (compound *II* in Scheme 1), the latter being most likely the proper source of the catalytically active species. The reduction proceeds via formation of bis($h^5$-cyclopentadienyl)chlorotitanium(III) eventually bis($h^5$-cyclopentadienyl)alkyltitanium(III) complex[16], and for the dimer, a series of structures have been proposed, some of which being expected to exhibit catalytic activity.

In the presence of alkene, the complex *II* dissociates to two highly active monomer species *III* which' are proper catalytic particles. If this reaction is equilibrium process[17] and complex *IV* is present in negligible concentration, the half order in the catalyst can be predicted, in accordance with the observed situation. With respect to the negative value of activation entropy, one can assume that the rate determining step involves the higher organized system and that the coordination (either alkene or hydrogen) is thus rate determining. As the initial reaction rate does not depend on hydrogen concentration, depends by first order on alkene and is further strongly dependent on alkene structure we are inclined to believe that the rate determining step is coordination of alkene to form complex *IV*.

The absence of isomerization of the alkene indicates that complex *IV* is fastly attacked irreversibly after rate determining step, so that the coordinated alkene has not time enough to C=C double bond migration. This idea is also supported by the observed independence of the reaction rate on hydrogen concentration. Hydrogen attack results in formation of alkane and regeneration of complex *III*, which closes the catalytic cycle.

## EPR *Spectra of Heterogenized Complexes*

With the aim of obtaining further information about catalytically active species we have studied spectroscopically homogeneous and heterogenized systems of the type A ($m = 0, 1$, and 3)



*A*

under conditions which simulated as close as possible the hydrogenation. In addition, the reaction of titanium(IV) complexes with individual reactants was also examined. The reduction of the heterogenized complex was performed in solution, the liquid and solid phase were separated and their EPR spectra separately recorded.

The solution of the bis($h^5$-cyclopentadienyl)dichlorotitanium(IV) complex reduced with 1-butyllithium, as well as the liquid phase separated after the reduction of heterogenized complexes did not contain EPR-active species. This agrees with the fact that "naked" titanium complexes undergo usually dimerization (if possible) to form inactive fulvalene complexes[12].

By contrast, the measurements of the solid phase of the reduced heterogenized complexes gave anisotropic EPR spectra which can be divided to two groups: those yielding $g_I$ values 1·999 up to 2·007 and those yielding $g_{II} = 1·933$ up to 1·945. These anisotropic spectra can be ascribed to stabilized $Ti^{3+}$ complexes since $Ti^{2+}$ compounds do not give EPR signal at room temperature. The prerequisite for formation of EPR signal was the presence of the reducing agent. Dependence of the spectrum on the titanium to the reducing agent ratio is depicted in Fig. 1. The Ti : Li value equaling to 1 : 10 which is necessary for maximum signal agrees well with the same ratio which is required for optimum course of the hydrogenation catalysed by both homogeneous and heterogenized titanium complexes. However, the excess of the reducing agent does not reduce $Ti^{3+}$ to $Ti^{2+}$ complexes.

The typical features of the EPR spectrum were not affected by the presence of hydrogen or alkene and anisotropic spectra cannot be ascribed to single, actual structures nor confronted with the number of cyclopentadiene rings or methylene groups.

The anisotropic character of the spectrum allows to judge that $Ti^{3+}$ complex is not likely bound to the surface via a free rotating bond (in such a case the spectrum would be isotropic), but that the rotation is restricted by another bonding which
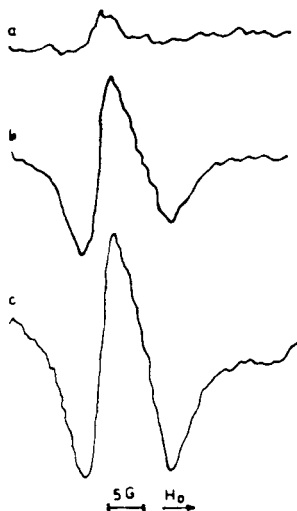


FIG. 1

Dependence of EPR signal on the titanium to reducing agent molar ratio used in the activation of the heterogenized $SiO_2$–CpTi($Cl_2$)Cp system. a Ti : Li = 1 : 3, b Ti : Li = 1 : 5, c Ti : Li = 1 : 10

can be either strong chemisorption or interaction with the free hydroxyl group or with the free electron pair of the siloxane bond. In this connection it is worth mentioning that Brubaker[16] found isotropic EPR spectrum on measuring the reduced titanium(IV) complex bound to an organic support, the surface of which provides lesser possibility of chemisorption. Interaction with the surface could account for the enhanced stability and lowered activity of catalytic species, the fact already stated in connection with the results of kinetic measurements of the activity of homogeneous and heterogenized systems (to obtain comparable $r^0$ under otherwise identical conditions, almost tenfold amount of the heterogenized titanium(IV) precursor had to be used compared to the homogeneous catalyst).

## Hydrogenation Catalyzed by Heterogenized Complexes

The catalytic activity of heterogenized systems was tested by the same way as in the case of bis(cyclopentadiene)dichlorotitanium(IV) complex. In this case, however, the catalytic activity has not been affected by the sequence in which the reactants were added. We have tested the activity of Ti(IV) complex and of complexes of the general formula $A$ ($m = 0, 1,$ and 3) which differed in the lenght of the spacer, after their reduction with butyllithium (optimum Ti : Li ratio was again 1 : 10). For each system, the dependence of the initial reaction rate on catalyst amount was determined, along with reaction orders in the alkene and hydrogen (Table I).

The rate constants calculated from the dependence of the reaction rate on catalyst amount, hydrogen partial pressure and alkene concentration were in good agreement with each other and did not differ more than by 10 per cent. Dependence of the initial reaction rate on the structure of alkenes was found to be similar to that for homogeneous catalysed hydrogenation, described already in this paper. In both

TABLE I

Rate constants and reaction orders for hydrogenation of 1-octene catalyzed by reduced $SiO_2-$ $-(CH_2)_m CpTi(Cl_2)Cp$ complexes

| | Reaction order[a] | | $k^b$ |
|---|---|---|---|
| $m$ | in alkene | in hydrogen | $1\ mol^{-1}\ s^{-1}$ |
| 3 | 1·07 | 0 | 0·75 |
| 1 | 1·00 | 0 | 2·93 |
| 0 | 0·98 | 0 | 3·26 |

[a] Reaction temperature 60°C, Ti : Li molar ratio = 1 : 10; [b] $r^0$ is linearly dependent on catalyst amount

cases the most reactive were 1-alkenes, internal alkenes not being hydrogenated. Similarly, also here isomerization of the unreacted alkene did not take place.

With the most efficient heterogenised system ($m = 0$, $c_{cat} = 0\cdot02$ mol Ti l$^{-1}$, $c_{octene} = 0\cdot583$ mol l$^{-1}$, $p(H_2) = 94\cdot1$ kPa), dependence of the initial reaction rate $r^0$ (mol H$_2$ s$^{-1}$ mol$^{-1}$ Ti) on temperature was determined: for temperatures 10, 20, 30, 40, 50, and 60°C the rate constants were successively 0·372, 0·952, 0·786, 1·104, 1·524, and 2·124. Based on these data, the activation enthalpy $\Delta H^{\neq}$ was calculated to be 26·84 J mol$^{-1}$ and the activation entropy $\Delta S^{\neq} = -112\cdot9$ J mol$^{-1}$ K$^{-1}$.

From the preceding discussion it is evident that the course of hydrogenation of alkenes catalyzed by the reduced homogeneous and heterogenized bis($h^5$-cyclopenta-dienyl)dichlorotitanium(IV) complex is the same or at least very similar, as far as the optimum titanium to the reducing agent ratio, the low activation energy and the relatively high negative entropy, the effect of alkene structure, the absence of competitive isomerization, first order in the alkene and zero order in hydrogen are concerned.

On the other hand, the difference has been found in the dependence of $r^0$ ($-dc_{alkene}/dt$) on the amount of the catalyst. While in the homogeneous system, the initial reaction rate depends by half-order on the catalyst concentration, in the heterogenized systems (at $V = $ const.) the reaction rate increases linearly with increasing amount of the catalyst, in accordance with the relation for reaction rate in heterogeneously catalysed batch reactor[18]. This fact documents that the catalytic cycle does proceed on the surface of solid phase and that the titanium(IV) complex does not leach to the solution. Of course, no conclusions can be made, however, concerning formation of the catalytically active species.

From qualitative findings (first order in the alkene, zero order in hydrogen, absence of isomerization, dependence of $r^0$ on alkene structure) we conclude that also in heterogenized systems the reaction procceds via a similar mechanism as in the case of homogeneous catalysts (i.e. it involves the initial coordination of alkene followed by fast hydrogen attack), providing that "naked" titanium complexes bound to the surface have limited possibility of mutual interaction, which is most likely the main reason of the nonstability of homogeneous systems[12]. That is why we were able to use any sequence of charging the alkene and reducing agent in heterogenized systems, while in the case of homogeneous analogue the "naked" titanium complex formed had to be stabilized by the presence of alkene. The mutual interaction of the two surface-bound intermediates of "naked titanium" becomes more probable with the higher mobility and length of the spacer between titanium complex and support surface. We have therefore investigated the activity of heterogenized catalysts in dependence on the number of methylene groups between the cyclopentadienyl substituent and silicon atom.

The results presented in Table II agrees with above idea, since the least active is the catalytic system in which titanium is bound to the surface via a long and mobile
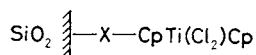
3-(cyclopentadienyl)propyl group (catalyst 33) and the most active is that in which the cyclopentadienyl group is bound directly to the silicon (catalyst 03).

When catalytic activity is examined in dependnece on the number of methyl groups on silicon (catalyst 03 vs. 02 and 01, eventually catalyst 03/Cl vs 02/Cl and 01/Cl) results given in Table II show that the catalyst activity slightly decreases with increasing number of methyl groups. Also in this case the activity decrease can be accounted for by the increasing mobility of the complex bound to the surface, and thus by the easier interaction of two catalytic centres; the cyclopentadienyl(di-methyl)silyl group is bound to the surface only by one siloxane bond and is thus more mobile than the cyclopentadienyl(methyl)silyl or cyclopentadienylsilyl groups bonded by two or three siloxane bonds.

On the other hand, comparison of the activity of complexes bonded to the silica functionalized by cyclopentadienyl-substituted silanes containing either chloro or ethoxy group (catalysts 03 vs. 03/Cl; 02 vs 02/Cl; 01 vs 01/Cl) show that the differences in the activity of these catalysts are very small. However, in all cases, the more active are the catalysts which were bound to the support treated with ethoxy--substituted silanes — most likely because of the adsorption of trace amounts of

TABLE II

Dependence of rate constant $k$ of hydrogenation of 1-octene on the spacer in the complex

$$SiO_2 \quad -X-CpTi(Cl_2)Cp$$

(catalyst amount 0·06 mmol Ti, $c_{alkene}$ = 0·291 mol l$^{-1}$, $p(H_2)$ = 96·16 kPa, $t$ = 60°C, $V$ = 12 ml, Ti : Li molar ratio = 1 : 10)

| Catalyst[a] | Spacer X | Method of synthesis[b] | Ti content mass % | $k$ l mol$^{-1}$ s$^{-1}$ | $\Delta k^c$ |
|---|---|---|---|---|---|
| 33 | ⩾Si–(CH$_2$)$_3$– | Et | 1·01 | 0·75 | |
| 13 | ⩾Si–CH$_2$– | Et | 1·09 | 2·93 | |
| 03 | ⩾Si– | Et | 1·28 | 3·26 | |
| 03/Cl | ⩾Si– | Cl | 0·5 | 2·88 | 0·36 |
| 02 | >Si(CH$_3$)– | Et | 0·96 | 3·03 | |
| 02/Cl | >Si(CH$_3$)– | Cl | 0·62 | 2·79 | 0·24 |
| 01 | –Si(CH$_3$)$_2$– | Et | 0·79 | 2·81 | |
| 01/Cl | –Si(CH$_3$)$_2$– | Cl | 0·71 | 2·71 | 0·10 |

[a] Cf. ref.[9]; [b] Et-support prepared with the use of ethoxysilanes, Cl-support by using chlorosilanes; [c] difference between rate constants for the catalysts prepared by using ethoxysilanes and chlorosilanes.

hydrogen chloride on the support on its treatment with chlorosilanes. Hydrogen chloride can affect unfavourably the behaviour of the catalyst. This assumption is supported by our finding that the activity decrease is the more distinct, the greater number of chlorine atoms are in the cyclopentadienylsilanes used to support treatment (see $\Delta k$ in Table II).

Heterogenization of bis(cyclopentadienyl)dichlorotitanium(IV) complex made it possible to separate liquid and solid phase used again separately in batch under the same conditions. While the liquid phase used did not catalyze hydrogenation, the solid phase containing used heterogenized catalyst turned out to be a good catalyst for the above hydrogenation. At the same time the decrease in the reaction rate when compared to the first use was very small (after three cycles approximately 6 per cent, Table III). The catalyst proper remains thus firmly bonded to the support and no leaching caused by the action of the reaction components to solution is taking place during hydrogenation.

TABLE III

Dependence of $r^0$ and conversion on reuse of the heterogenized system (03) in hydrogenation of 1-octene (catalyst amount 0·062 mmol Ti, $c_{alkene} = 0.291 \text{ mol l}^{-1}$, $p(H_2) = 96.14 \text{ kPa}$, $t = 60°C$, $V = 12 \text{ ml}$)

| Use | $r^0$, mol H$_2$ s$^{-1}$ mol$^{-1}$ Ti | Conversion (%) after 15 min |
|---|---|---|
| First | 1·19 | 78 |
| Second | 1·14 | 75 |
| Third | 1·12 | 69 |
| Fourth | 0·77 | 53 |

The just mentioned small decrease in the catalytic effectiveness of heterogenized complexes on their reuse is most likely caused by impurities transferred into the system during separation and reuse of the catalyst. We believe that this phenomenon could be prevented by performing hydrogenation as a continuous process.

Summarizing, the reduced immobilized bis(cyclopentadienyl)dichlorotitanium(IV) complexes are highly efficient hydrogenation catalysts. These remain firmly bonded to silica in the course of hydrogenation as well as during the subsequent handling and are not thus leached from the support by the action of other reaction components. They exhibit higher activity than the so far most frequently used heterogenized rhodium complexes.

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