

## HYDROGENATION AND ISOMERISATION OF UNSATURATED COMPOUNDS ON A PALLADIUM CATALYST

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Received October 10th, 1979

Catalytic hydrogenation and simultaneous isomerisation of 1- and 2-hexene and of three unsaturated alcohols was studied under normal conditions on a palladium catalyst. The effect of solvents and of substrate structure on the course of this reaction is reported. The structure of the starting compound was found to have dominant effect on the selectivity of hydrogenation while solvents influenced significantly the reaction rate and selectivity of competition reactions of 1-hexene and unsaturated alcohols.

Liquid phase hydrogenation of unsaturated substrates has been extensively studied. Most of the works deal with the effect of catalyst, solvent, substrate structure and reaction conditions on the kinetics and stereospecificity of hydrogenation reactions. The detailed knowledge of relations between substrate structure, solvents and the course of hydrogenation has been reported so far only for platinum catalysts<sup>1-5</sup>. While on these catalysts the reaction course is not complicated by side reactions, hydrogenations of olefinic substrates on palladium catalysts are often accompanied by double bond isomerisation<sup>6-8</sup> which in the case of unsaturated alcohols can produce aldehydes and ketones<sup>9-17</sup>. In some cases also dehydration or hydrogenolysis of hydroxyl group has been observed<sup>11</sup>.

With platinum catalysts it was found that the values of reaction rates, relative adsorption coefficients of substrates and selectivities in competition hydrogenation depend not only on the structure of reactants but also on the composition of the liquid phase<sup>2-5</sup>. The most important changes in the selectivities of competition reactions can be achieved<sup>2</sup> in systems of structurally different compounds (unsaturated alcohol-olefin). These changes can be caused by the presence of unsaturated substrate and also by solvents<sup>3-5</sup>. While the unsaturated substrate changes the selectivity of hydrogenation by adsorption on catalyst surface and by interactions from the volume phase with the molecules adsorbed on the catalyst, the solvent does not compete with substrate in adsorption but acts only *via* interactions from the volume phase. Majority of these experimental facts have been successfully quantified<sup>2-5</sup>.

In order to obtain the more detailed information, in the present work we have examined the above mentioned effects in systems having substantially more complex kinetics.

### EXPERIMENTAL

*Compounds used.* 1-Hexene, 2-methyl-3-buten-2-ol, a mixture of 59.3% of *cis*- and 40.7% of *trans*-2-hexene, 1-heptene-4-ol (all Koch-Light, England). 2-Hepten-4-ol was prepared by reaction

of crotonaldehyde with propylmagnesium bromide<sup>18</sup> in 73% yield (b.p. 54–56°C/1.67 kPa). Cyclohexane and methanol (analytical purity grade) were commercial samples (Lachema, Brno). All the compounds were freshly distilled and were chromatographically pure. The catalyst was 3% Pd on activated carbon — Supersorbon Degussa (Cherox 41—00, Chemické závody ČSSP, Záluží), the fraction used had particle size <0.05 mm. Hydrogen (electrolytic, Technoplýn. Kyje) was used as obtained in pressure cylinders.

**Apparatus and procedure.** Hydrogenations were carried out<sup>5</sup> in a discontinual, isothermic, ideally mixed reactor at 20°C and under atmospheric pressure. The reaction mixture contained 0.09 g of the catalyst and 1.6 ml of equimolar mixture of two olefinic substrates (or of only one substrate) or the same amount (by volume) of olefins and solvents. In the course of the reaction the samples of the reaction mixture were withdrawn and analyzed gas chromatographically.

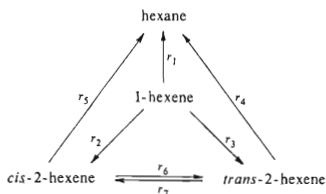
**Analytical methods.** The samples were analysed on Chrom 4 instrument equipped with a flame ionisation detector, using a glass column (4 m × 2.5 mm) filled with 15% PEG 1540 on Chromosorb P (25—80 mesh). Analyses of the mixtures from competition hydrogenation of an olefin with an unsaturated alcohol were performed at two temperatures; at 48°C in the analysis of olefins and their hydrogenation products and at 149°C in the analysis of unsaturated alcohols and their products. Substances having the same carbon skeleton were presumed to show the same relative response.

## RESULTS AND DISCUSSION

All measurements were carried out under conditions which ensured that the reaction rate is not influenced by mass transport. The compounds subjected to hydrogenation were 1-hexene, a mixture of *cis*- and *trans*-2-hexene, 1-hepten-4-ol, 2-hepten-4-ol, 2-methyl-3-buten-2-ol and an equimolar mixture of 1-hexene with 1-hepten-4-ol or with 2-methyl-3-buten-2-ol and that always *in substantia* (*i.e.* without solvent) and further in methanol and in cyclohexane.

### Hydrogenation of Individual Substrates

Fig. 1 shows time dependence of concentrations of individual components of the reaction mixture for hydrogenation of 1-hexene in the absence of solvent ( $c$  is the dimensionless concentration expressed as the ratio of the concentration of the component in time  $t$  to the initial concentration of the corresponding substrate,  $t$  is time (in min)). It can be assumed that the reactions proceed<sup>8</sup> according to Scheme 1.



SCHEME 1

In hydrogenation of a mixture of approx. 60% of *cis*- and 40% of *trans*-2-hexene formation of 1-hexene and 3-hexenes was not found to take place. The concentration of *trans*-2-hexene increased in the initial phase of the reaction and after attaining 65% it began to decrease. This was caused both by the lower reactivity of this isomer in hydrogenation<sup>8</sup> and by its formation by simultaneously proceeding isomerisation of *cis*-2-hexene.

Scheme 1 is a simplified example of the general scheme of mutual transformations taking place in hexene-hexane systems. This simplification is given by experimental finding that none of the reaction mixtures contained 3-hexenes, similarly as 1-hexene was not formed in hydrogenation of 2-hexenes.

The dependences obtained for hydrogenation of 1-hexene made it possible to determine the values of initial rates  $r_1 - r_3$  which are presented in Table I. Hydrogenations and isomerisations were fast in methanol, slower in cyclohexane and slowest in the system without solvent. A similar trend was reported also for hydrogenation of unsaturated ethers<sup>19</sup>.

The ratio of the *trans*- to *cis*-2-hexene concentration in the maximum of these intermediate products equaled to 2 in hydrogenation of 1-hexene *in substantia* and in methanol and was equal to 2.6 in the reaction carried out in cyclohexane. The magnitude of this ratio reflects the rate of formation and transformation of both isomers. The effect of solvent on this ratio was not too significant.

The selectivity of the reaction was defined as the ratio of hydrogenation to isomerisation rates  $r_1/(r_2 + r_3)$ . This ratio expresses that of the reaction rates of side

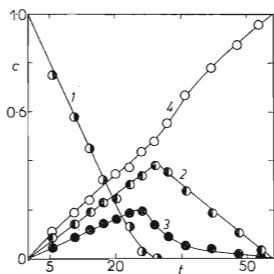


FIG. 1

Course of Hydrogenation of 1-Hexene

1 1-Hexene, 2 *trans*-2-hexene, 3 *cis*-2-hexene, 4 hexane.

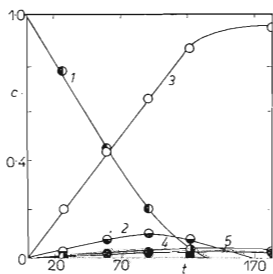


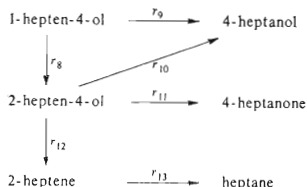
FIG. 2

Course of Hydrogenation of 1-Hepten-4-ol

1 1-Hepten-4-ol, 2 2-hepten-4-ol, 3 4-heptanol, 4 4-heptanone, 5 heptane.

reactions having similar mechanism and kinetics<sup>1</sup>. It can be assumed that adsorption coefficients of the starting compound for both reactions are identical and hence the ratio of the reaction rates corresponds to the ratio of the rate constants. The results are summarised in Table III. Also here the effect of solvent was not significant.

Fig. 2 shows time dependence of concentrations of individual components of the reaction mixture for hydrogenation of 1-hepten-4-ol in the absence of solvent. One can expect that the reactions proceed according to Scheme 2. Formation of side



SCHEME 2

products can be explained by double bond migration and by hydrogenolytic reactions. 2-Hepten-4-ol arises from 1-hepten-4-ol apparently by double bond migration to the thermodynamically more stable position. Its further migration between carbon atoms adjacent to the carbon substituted with OH group leads to formation of the enol form of 4-heptanone. This reaction is obviously analogous to the formation of propionaldehyde in hydrogenation of allyl alcohol on palladium catalysts<sup>11</sup>. The presence of 4-heptanone in the reaction mixture was confirmed by IR spectroscopy. Under experimental conditions used, the rate of the hydrogenation of this compound is so slow that this substance appears to be one of the final products

TABLE I  
Initial Rates of Individual Reactions in Hydrogenation of 1-Hexene

Reaction rate <sup>a</sup>	Initial reaction rate, mmol min <sup>-1</sup> g <sub>cat</sub> <sup>-1</sup>		
	<i>in subst.</i>	methanol	cyclohexane
$r_1$	2.42	4.74	3.20
$r_2$	1.15	3.75	1.79
$r_3$	1.90	5.38	2.82

<sup>a</sup> Designation see Scheme 1.

in Scheme 2. Formation of heptane can be most likely explained by hydrogenolysis of 2-hepten-4-ol which is hydrogenated under these conditions to heptane. In some cases we succeeded in detecting 2-heptene in the reaction mixture (however, in hydrogenation of 1-hepten-4-ol in methanol and in cyclohexane this alkene could not be determined analytically, having the same retention time as the solvent).

Hydrogenolysis of 1-hepten-4-ol to 1-heptene, the hydrogenation of which could yield also heptane, seems to be less probable. Under mentioned reaction conditions saturated secondary alcohols did not undergo hydrogenolysis. The observed phenomenon is thus caused by the presence of the double bond in alcohol molecule. One can therefore expect that the influence of this bond will decrease with increasing distance between the bond and the hydroxyl group.

Fig. 2 was used to determine the values of initial reaction rates  $r_8$  and  $r_9$  and analogously were also determined the values of  $r_{10} - r_{12}$  constants from hydrogenation of 2-hepten-4-ol (Table II). The reaction proceeded at a fastest rate in cyclohexane and were slowest in the absence of solvents. The values of selectivities for 1-hepten-4-ol ( $r_9/r_8$ ) and 2-hepten-4-ol ( $r_{10}/r_{11}$ ), defined similarly as in the case of 1-hexene, are given in Table III. While 1-hexene underwent isomerisation more easily than hydrogenation under all the conditions used, both unsaturated alcohols were preferentially hydrogenated. Compared to the reaction without solvent, the values of selectivity were lower in its presence, with the exception of hydrogenation of 2-hepten-4-ol in cyclohexane. The ratio of hydrogenation to isomerisation rates is determined obviously by the stability<sup>20</sup> of the so called "semihydrogenated state", which is given by co-action of the structure and solvent effects. The selectivity is determined above all by the structure of the starting compound, the effect of solvent not being dominant.

TABLE II

Initial Rates of Individual Reactions in Hydrogenation of 1- and 2-Hepten-4-ol

Reaction rate <sup>a</sup>	Initial reaction rate, mmol min <sup>-1</sup> g <sub>cat</sub> <sup>-1</sup>		
	<i>in subst.</i>	methanol	cyclohexane
$r_8$	0.15	0.37	0.63
$r_9$	0.94	1.61	1.88
$r_{10}$	0.30	0.41	0.59
$r_{11}$	0.06	0.09	0.08
$r_{12}$	0.03	0.31	— <sup>b</sup>

<sup>a</sup> For designation see Scheme 2; <sup>b</sup> not determined for analytical reasons.

Hydrogenation of 2-methyl-3-buten-2-ol to 2-methyl-2-butanol was selective under all the conditions used. Initial rates of the hydrogenation carried out in the absence of solvent, in methanol and in cyclohexane were 0.45, 0.48 and 0.82 mmol . min<sup>-1</sup> . g<sub>cat</sub><sup>-1</sup> respectively. Table III summarises also the values of reactivity on individual substrates which was expressed as the total rate of transformation of these substrates by the sum of initial rates of individual steps). Data document that 1-hexene exhibits the highest reactivity. From the unsaturated alcohols the most reactive was 1-heptene-4-ol, *i.e.* the alcohol with monosubstituted double bond. 2-Methyl-3-buten-2-ol, branched on the carbon adjacent to the bond (which is thus more hindered sterically) showed lower reactivity. The least reactive was 2-hepten-4-ol, having disubstituted double bond. These conclusions comport qualitatively, with the effect of the structure of unsaturated alcohols on the rate of their hydrogenation on platinum catalysts<sup>2</sup>.

In all cases the presence of solvent led to increased reactivity of substrates. The reactivity of unsaturated alcohols was higher in cyclohexane while that of 1-hexene in methanol. This effect may be ascribed to interactions of solvent from the volume phase with substrate molecules adsorbed on the catalyst surface (see later). Solvents affected more the reactivity of individual substrates than the selectivity of their hydrogenation. This is apparently the result of very strong effect of solvents on the strength of the bond between the substrate and the catalyst. Formation of isomeric substance and the saturated product proceeds *via* the same transition state<sup>20</sup> and the direction of further transformation of this intermediate product is not so sensitive toward solvent action.

#### *Competitive Hydrogenation of Olefins and Unsaturated Alcohols*

In Figs 3 and 4 are represented graphically time dependences of concentrations of individual substances for competition hydrogenation of 1-hexene with 1-hepten-4-ol or with 2-methyl-3-buten-2-ol without solvent. The above dependences were used to determine the selectivities<sup>21</sup> defined as the ratio of the reactivity of both starting substrates. Experiments which were carried out with the use of methanol and cyclohexane as solvents were analysed in the same way. Despite of the great complexity of systems where a number of reactions are taking place, the relationships between logarithms of actual concentrations of the starting substrates were linear. This confirms the validity of the method used for selectivity determination. This fact can be most likely attributed to the fact that denominators of the fractions expressing the reaction rate in the form of Langmuir-Hinshelwood equations are reduced in competition reactions and hence further compounds formed by side reactions do not affect the ratio of reactivities of starting substrates. Selectivity values are presented in Table IV. They demonstrate that the selectivity for the unsaturated alcohol-olefin system is lower in methanol and higher in cyclohexane, compared

to the system without solvent. The same results were obtained on platinum catalysts<sup>2,4</sup> which catalyse only hydrogenation reactions. Polar solvents increase the relative reactivity of the polar substrate and *vice versa*, which is caused evidently by their interactions from the volume phase with adsorbed substrate molecules<sup>2,4</sup>. As mentioned above, the effect of solvents on the rate of transformation of substrates as such was in accordance with this observation. In the 1-hexene-2-methyl-3-buten-2-ol system the olefin was more reactive in all cases, similarly as in the system with 1-hepten-4-ol in *substantia* and in methanol; in cyclohexane 1-hexene was even more reactive than 1-hepten-4-ol.

Time dependences of concentrations of individual substances in competition hydrogenation allow to observe an interesting effect of each one of the unsaturated substrates on the ratio of the rates of hydrogenation to isomerisation of the other substrate. Table V summarises the values of selectivities expressed as the ratio of hydrogenation to isomerisation rate of 1-hexene in the presence of 2-methyl-3-buten-2-ol and 1-hepten-4-ol, along with the values of selectivities expressed by the analogous ratio of the rates of transformations of 1-hepten-4-ol in the presence of 1-hexene. These values were obtained from initial reaction rates of hydrogenation and isomerisation. For purposes of mutual comparison the Table contains also the selectivity

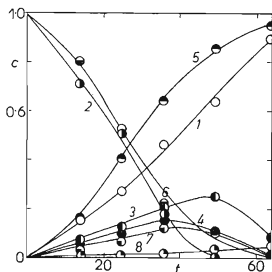


FIG. 3

Competition Hydrogenation of 1-Hexene with 1-Hepten-4-ol

1 Hexane, 2 1-hexene, 3 *trans*-2-hexene, 4 *cis*-2-hexene, 5 4-heptanol, 6 1-hepten-4-ol, 7 2-hepten-4-ol, 8 4-heptanone.

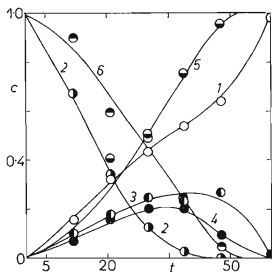


FIG. 4

Competition Hydrogenation of 1-Hexene with 2-Methyl-3-buten-2-ol

1 Hexane, 2 1-hexene, 3 *trans*-2-hexene, 4 *cis*-2-hexene, 5 2-methyl-2-butanol, 6 2-methyl-3-buten-2-ol.

TABLE III  
Selectivities of Hydrogenation and Total Reactivities of Substrates

Substrate	Selectivity/Reactivity <sup>a</sup>		
	<i>in subst.</i>	methanol	cyclohexane
1-Hexene	0.79/5.47	0.52/13.87	0.69/7.81
1-Hepten-4-ol	4.80/1.09	3.63/1.98	2.72/2.51
2-Hepten-4-ol	5.30/0.36	4.61/0.49	7.74/0.66
2-Methyl-3-buten-2 ol	∞/0.45	∞/0.48	∞/0.82

<sup>a</sup> Selectivity is given by the ratio of hydrogenation to isomerisation rate, the reactivity ( $\text{mmol} \cdot \text{min}^{-1} \text{g}_{\text{cat}}^{-1}$ ) is given by the sum of both rates.

TABLE IV  
Selectivities of Competition Reactions for Unsaturated Alcohol-Olefin Systems

System	Selectivity		
	<i>in subst.</i>	methanol	cyclohexane
2-Methyl-3-buten-2-ol/1-hexene	0.34	0.13	0.76
1-Hepten-4-ol/1-hexene	0.87	0.25	1.60

TABLE V  
Selectivities of Hydrogenation in the Presence of Another Unsaturated Substrate

Starting substrate	Influencing substrate	Selectivity <sup>a</sup>					
		<i>in subst.</i>		methanol		cyclohexane	
		A	B	A	B	A	B
1-Hexene	2-methyl-3-buten-2-ol	0.79	1.02	0.52	0.86	0.69	0.90
1-Hexene	1-hepten-4-ol	0.79	1.08	0.52	0.69	0.69	1.02
1-Heptene-4-ol	1-hexene	4.80	3.83	3.63	4.68	2.72	6.46

<sup>a</sup> A the values obtained in hydrogenation of the starting substrates, B the values obtained in hydrogenation of the starting substrate in the presence of another influencing substrate.



values determined for hydrogenation of individual substrates from Table III. It is evident that in all cases the unsaturated alcohols increase the ratio of hydrogenation to isomerisation rate of 1-hexene. On the other hand, the presence of 1-hexene leads to an increase in the ratio of hydrogenation to isomerisation rate of 1-hepten-4-ol in methanol and in cyclohexane, while in the hydrogenation *in substantia* this ratio is decreased. This documents that the presence of another unsaturated substrate, competitively adsorbed on the catalyst surface, influences the stability of transition "semihydrogenated" state of the substrate, transformations of which are investigated. However, to formulate more general conclusions, more experimental data are needed.

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Translated by J. Hetflejš.