

MODEL REACTIONS FOR THE STUDY OF HYDROGENATION AND ACIDIC ACTIVITY OF PALLADIUM CATALYSTS

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Palladium catalysts have been used to study the hydrogenation of 1-phenyl-2-butene-1-ol which is accompanied by several side reactions considered to be acid-catalysed. Another model reaction studied was dehydration and subsequent hydrogenation or hydrogenolysis of 1-phenyl-1,3-propanediol to 3-phenyl-1-propanol, accompanied by formation of propylbenzene. The dehydration and propylbenzene formation can be again classified as acid-catalysed reactions. Another one is methanolysis of styrene oxide taking place under conditions of liquid phase hydrogenation due to the acid properties of Pd-H systems. Hydrogenation activity of Pd catalysts was tested by hydrogenation of cyclohexene. Sixteen Pd catalysts on different supports and with different content of active component were used, their activity and selectivity was determined and the effect of variable parameters in the synthesis of these catalysts on the activity and selectivity is discussed.

In studies^{1,2}, the reactions taking place on Pd catalysts only in the presence of hydrogen, although stoichiometrically its presence is not demanded, have been summarized. These reactions are usually catalysed by protonic catalysts, which supports the assumption that some forms of hydrogen activated by palladium exhibit to some extent protonic character^{3,4}.

In this work we used the three, so far not described model systems that were chosen so that they made it possible to express hydrogenation or acidic activity of Pd catalysts in the presence of hydrogen. In all the systems, the reactions belonging to the class of acid-catalysed reactions have been taking place. Standard test reaction for determining hydrogenation activity was hydrogenation of cyclohexene that proceeded without side reactions.

EXPERIMENTAL

Catalysts used. The catalysts used in this study are summarized in Table I. Catalysts 13, 14, and 15 were commercial samples (13, 14 — Koch-Light, England, 15 — Farmakon Olomouc, Czechoslovakia), the others were prepared in connection with this study by impregnation of the support with palladium(II) chloride solution, followed by the reduction, using procedure given

in Table I. The modification of the catalysts was made with aqueous potassium carbonate solution that was used in such amount that ensured 10 wt. % content of K_2CO_3 (with respect to weight of palladium) in all the modified palladium catalysts.

Compounds used. 1-Phenyl-2-butene-1-ol was prepared by reaction of crotonaldehyde with phenylmagnesium bromide and subsequent hydrolysis of the adduct formed⁵. 1-Phenyl-1,3-propanediol was obtained by acidolysis of 4-phenyl-1,3-dioxane with acetanhydride followed by hydrolysis of the diacetate formed⁶. Styrene oxide was prepared by reaction of styrene with cumene hydroperoxide in the presence of a molybdenum catalyst⁷. Cyclohexene was obtained by dehydration of cyclohexanol on γ -alumina⁸. All the model substances were distilled before use and were chromatographically pure. Hydrogen was electrolytic, according to ČSN 654435 (Technoplyn, Prague) and was used without further purification.

Apparatus and measurements. Hydrogenations were carried out in a standard apparatus⁹ which consisted of a magnetically stirred glass reactor and gas burette. Hydrogenolysis of 1-phenyl-1,3-propanediol and methanolysis of styrene oxide were carried out isothermally in a glass, magnetically stirred reactor provided with a reflux condenser, a sampling probe and hydrogen inlet under the level of reaction mixture.

TABLE I
Catalysts used

No.	Pd content wt. %	Support	Procedure	
			Reducing agent	Reduction temp., °C
1	3	charcoal ^a	CH ₂ O	100
2	5	charcoal ^a	H ₂	250
3	5	charcoal ^a	CH ₂ O	100
4	5	charcoal ^a	NaBH ₄	25
5	5	charcoal ^a	NH ₂ NH ₂	20
6	5	charcoal ^a	H ₂	100
7	10	charcoal ^a	CH ₂ O	100
8	10	charcoal ^a	H ₂	250
9	5	graphite	CH ₂ O	80
10	5	SiO ₂	H ₂	250
11	10	SiO ₂	H ₂	250
12	5	Al ₂ O ₃	CH ₂ O	100
13	10	BaSO ₄	— ^b	— ^b
14	5	CaCO ₃	— ^b	— ^b
15	4.3	CaCO ₃ modified by Pb	HCOOH	80
16	100.0	no support	CH ₂ O	0

^a Activated; ^b data are not known.

dependences of hydrogen consumption at the origin, initial reaction rates of hydrogenation were determined and expressed in mmole H_2 per min g_{Pd} (Table II).

A characteristic course of reactions of 1-phenyl-2-butene-1-ol with the use of catalyst 6 (5% Pd-C, 100°C) is represented graphically in Fig. 1.

The final products of the hydrogenation of 1-phenyl-2-butene-1-ol on all the catalysts except those reduced with hydrogen were butylbenzene and 1-phenyl-1-butanol. When the catalysts reduced with hydrogen were applied, the above products were accompanied by 1-phenyl-3-butanol and 1-phenyl-3-methoxybutane in significant amounts. The hydroxy or methoxy group in position 3 with respect to the benzene ring results only from isomerization of the starting unsaturated alcohol. Hydrogenation of 1-phenyl-1-butene-3-ol yields 1-phenyl-3-butanol. Formation of 1-phenyl-3-methoxybutane can be explained by etherification of the hydroxyl group by methanol followed by hydrogenation of the formed 1-phenyl-3-methoxybutane.

The selectivity of the acid catalysed reaction was defined as the measure of acidic properties related to the total activity of catalyst, *i.e.* (% of butylbenzene + % of 1-phenyl-3-butanol + % of 1-phenyl-3-methoxybutane)/(% of butylbenzene + % of 1-phenyl-3-butanol + % of 1-phenyl-3-methoxybutane + % of 1-phenyl-1-butanol), as expressed by Eq. (1)

$$S(H^+) = 100 \frac{\sum H^+}{(\sum H^+ + H_2)}. \quad (1)$$

It was found that the support, active component content, and the procedure used in catalyst preparation do affect the rate, selectivity, and stoichiometry of the reactions taking place in the course of hydrogenation of 1-phenyl-2-butene-1-ol on Pd catalysts (Table II). To suppress their acidic properties, these catalysts were modified by potassium carbonate. The modification resulted in the decrease of the rate of hydrogenation of 1-phenyl-2-butene-1-ol by 5.5 up to 25.3 per cent. The activity decrease is understandable and is obviously caused predominantly by mechanical blocking of the Pd surface with potassium carbonate. The selectivity decrease (2.3–79.4%) was obviously caused by the decrease of the acid character of the Pd-H system due to K_2CO_3 .

The values of initial rates of hydrogenation of cyclohexene, r_1 , and of 1-phenyl-2-butene-1-ol, r_2 , were found to be interrelated by a linear relation (2)

$$r_2 = 8.43 + 0.45 r_1, \quad (2)$$

with the correlation coefficient $r_{x,y} = 0.76$, this value being higher than the critical value of the correlation coefficient for 1%-level of significance.

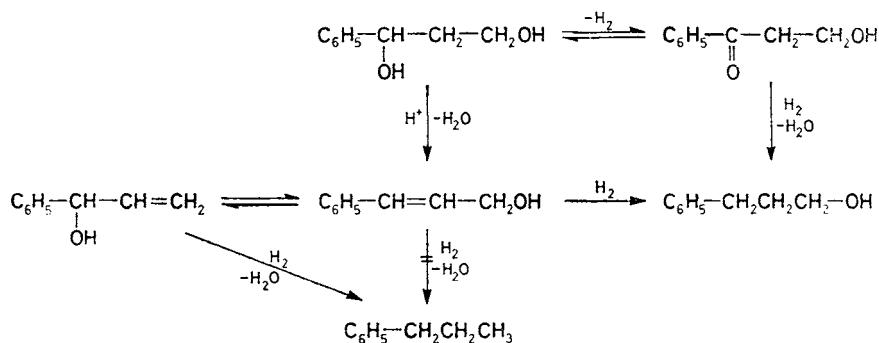
Other model reaction used to examine the properties of Pd-H systems was hydrogenolysis, resp. dehydration and subsequent hydrogenation of 1-phenyl-1,3-propanediol. Experimental data do not make it possible to discuss in more detail the mecha-

TABLE II
Kinetic data for model reactions on Pd catalysts

Catalyst	Hydrogenation of			Hydrogenolysis of			Methanolysis of styrene oxide		
	cyclohexene	1-phenyl-2-butene-1-ol	1-phenyl-1,3-propanediol	1-phenyl-1,3-propanediol	$S, \%$ ^b	$1/\tau_{0.5}$ ^a	2-phenyl-	subst. 2-methoxy-1-ethanol, % ^c	1-phenyl-
	$r1^a$	$r2^a$	$S(H^+), \%$	$r3^a$					
1	53.3	38.1	67.0	23.6	0	23.0	25.3	70.6	
2	—	21.5	75.6	27.4	0	25.8	100.0	0	
3	42.5	27.0	60.0	12.7	5	—	—	—	
4	43.0	24.2	61.0	5.6	7	—	—	—	
5	45.5	20.8	63.0	14.2	1	—	—	—	
6	41.7	19.4	86.0	9.6	9	—	—	—	
7	19.5	18.0	59.0	2.6	0	4.5	73.0	0	
8	—	16.3	69.4	18.4	5	—	—	—	
9	27.8	20.4	44.4	— ^d	0	14.5	15.9	83.3	
10	—	18.5	63.0	17.6	0	13.3	100.0	0	
11	—	12.1	55.7	6.6	0	6.7	81.3	0	
12	42.5	87.1	14.0	— ^d	0	12.5	84.6	0	
13	12.6	22.3	44.8	— ^d	0	6.8	70.0	0	
14	37.0	42.0	39.0	— ^d	0	— ^d	0.03	0	
15	4.1	10.0	42.0	— ^d	0	— ^d	6.7	0	
16	1.3	2.3	63.0	0.1	0	0.05	10.0	87.3	

^a $r1, r2$ (mmole $H_2 \text{ min}^{-1} \text{ g}_{Pd}^{-1}$), $r3$ (mmole 1-phenyl-1,3-propanediol $\text{min}^{-1} \text{ g}_{Pd}^{-1}$), $1/\tau_{0.5}$ ($\text{min}^{-1} \text{ g}_{Pd}^{-1}$), $1/\tau_{0.5}$ ($\text{min}^{-1} \text{ g}_{Pd}^{-1}$). ^b S = selectivity defined by the content of propylbenzene at the total conversion of 1-phenyl-1,3-propanediol. ^c Final composition. ^d Reaction proceeds very slowly.

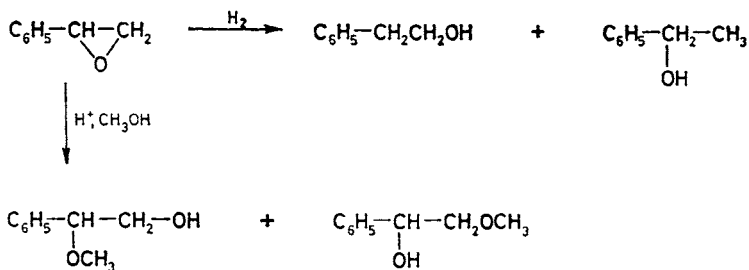
nism of water release from the molecule of 1-phenyl-1,3-propanediol. We may deal here with hydrogenolytic cleavage of the C—OH bond or with dehydration and subsequent hydrogenation. For purposes of simplification, in further text we use the term hydrogenolysis. The reaction was carried out in *n*-butanol at 100°C. With most of the catalysts, 3-phenyl-1-propanol was formed as the sole product. In the case of catalysts 3–6 and 8 the just mentioned alcohol was accompanied by propylbenzene and further by two intermediate products: 1-phenyl-1-propene-3-ol and 1-phenyl-3-hydroxy-1-propanone (Fig. 2). Their formation can be explained by Scheme 2. The values of initial reaction rates obtained by construction of tangents



SCHEME 2

at the origin to the experimental time dependences of 1-phenyl-1,3-propanediol consumption are presented in Table II. For the reaction just discussed, the active catalysts are essentially only those supported on activated carbon or silica gel. Separate experiments have shown that none of these supports as such catalyzes this reaction, so that the activity is induced by co-action of the active metal and support. This phenomenon is of interest and documents the important effect of the support on the properties of the active component even at the high content of the component on the support. Another important finding was the fact that in the course of heating of the catalysts in the reaction mixture to the reaction temperature in the absence of hydrogen, their properties were developed in such a way that the catalysts were several times more active than those used directly (by introducing the catalyst to the warmed-up reaction mixture). Modification of the catalysts by potassium carbonate resulted again in decrease of their activity which was greater than in the case of hydrogenation of 1-phenyl-2-butene-1-ol. This indicates that this reaction requires the more acidic catalyst.

The acidic properties of Pd-H systems were further studied in the methanolysis of styrene oxide, taking place under conditions of liquid phase hydrogenation according to Scheme 3. With the use of Pd catalysts, hydrogenation reaction did not



SCHEME 3

proceed and the reaction product was 2-phenyl-2-methoxy-1-ethanol, in several cases also 1-phenyl-2-methoxy-1-ethanol. It was found that the reaction shows an induction period (Fig. 3). Therefore, initial reaction rates were not determined from time dependences of concentrations of reaction mixture components but only half-times of the reactions were evaluated (Table II).

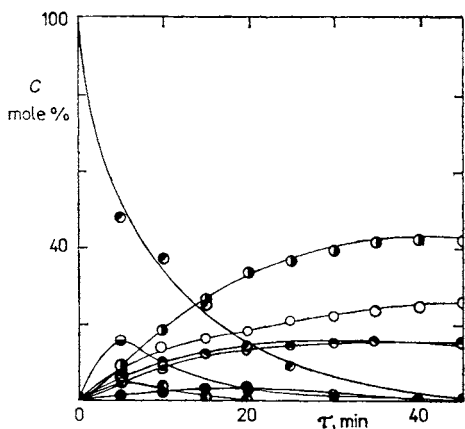


FIG. 1

Course of the reactions of 1-phenyl-2-butene-1-ol on catalyst 6 in methanol in the presence of hydrogen (*C* composition of reaction mixture, τ time). ● 1-Phenyl-2-butene-1-ol, ● 1-phenyl-1-butanol, ● 1-phenyl-3-methoxybutane, ○ butylbenzene, ● 1-phenyl-3-butanol, ● 1-phenyl-2-butene, ● 1-phenyl-1-butene-3-ol, ● 1-phenyl-3-methoxy-1-butene

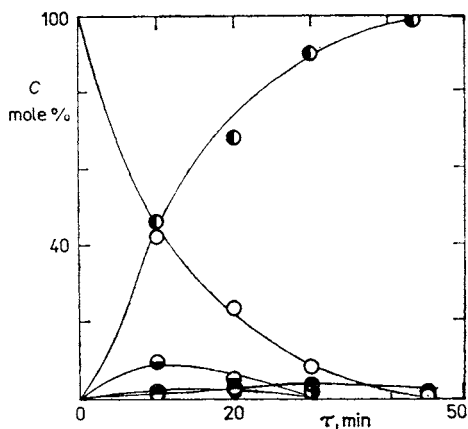


FIG. 2

Course of hydrogenolysis of 1-phenyl-1,3-propanediol on catalyst 5 in n-butanol at 100°C (*C* composition of reaction mixture τ time). ○ 1-Phenyl-1,3-propanediol, ● 3-phenyl-1-propanol, ● propylbenzene, ● 1-phenyl-3-hydroxy-1-propanone, ● 1-phenyl-1-propene-1-ol

Fig. 4 shows comparison of total relative activities of individual Pd catalysts for four model reactions under study. The activities are expressed in % of the activity of the most active catalyst for a given reaction. In the case of cyclohexene (r_1) and of 1-phenyl-2-butene-1-ol (r_2) we deal here with hydrogenation, in the case of 1-phenyl-1,3-propanediol (r_3) we deal with hydrogenolysis, resp. dehydration and subsequent hydrogenation, in the case of styrene oxide we deal with methanolysis, both latter reactions being acid-catalysed. It was found that the sequence of the activity of individual catalysts differs from each other, depending on the reaction studied. A certain relation has been found between reactions similar as far as their mechanism is concerned (hydrogenation of the double bond of cyclohexene and of 1-phenyl-2-butene-1-ol), while no relations have been found for the acid properties

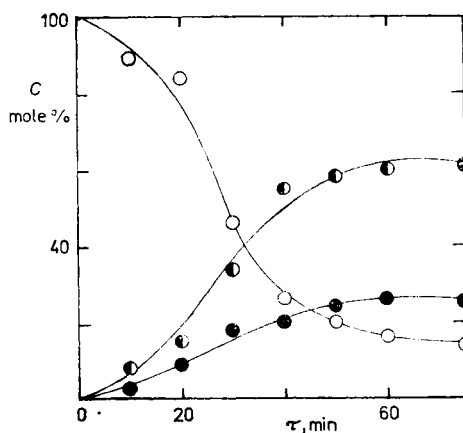


FIG. 3

Course of alcoholysis of styrene oxide on catalyst 1 (C composition of reaction mixture, τ time). \circ Styrene oxide, \bullet 2-phenyl-2-methoxy-1-ethanol, \bullet 1-phenyl-2-methoxy-1-ethanol

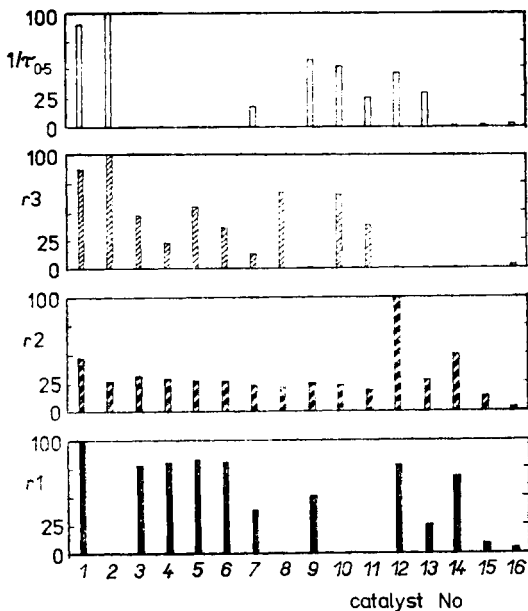


FIG. 4

Column diagram for comparison of relative activities of Pd catalysts. r_1 , r_2 and r_3 are relative initial reaction rates of hydrogenation of cyclohexene, 1-phenyl-2-butene-1-ol and of hydrogenolysis of 1-phenyl-1,3-propanediol (%). $1/\tau_{0.5}$ is the relative reciprocal value of half-time of the alcoholysis of styrene oxide (%)

of the catalysts (rates of the latter two reactions, the selectivity of acid-catalysed reactions in the hydrogenation of 1-phenyl-2-butene-1-ol).

The extreme dependences of the sensitivity of acid-base function on the composition and procedure of the reduction of catalyst found in this work cannot be thus abstracted from the given reaction. This makes it so far impossible to predict the activity of palladium catalysts for the systems differing more significantly from those studied experimentally.

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