HYDROGENATION OF CINNAMYL METHYL ETHER AND ALLYLBENZENE ON PALLADIUM CATALYSTS

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The hydrogenation of cinnamyl methyl ether and allylbenzene in hexane and acetone at 20°C and atmospheric pressure of hydrogen has been studied on eight palladium catalysts. The hydrogenation of cinnamyl methyl ether is accompanied by C—O bond splitting giving rise to propylbenzene and methanol, the hydrogenation of allylbenzene is associated with the isomerization of the double bond resulting in its conjugation with the benzene ring. A marked solvent effect on the selectivity of hydrogenation of cinnamyl methyl ether has been observed and ascribed to the effect of solvated protons on the adsorbed molecules of the ether which is promoted by polar medium. The solvent effect on the isomerization of allylbenzene during the hydrogenation is little pronounced, which suggests that this reaction is not of ionic nature.

The problem of bonding of hydrogen to metal surfaces is very complicated; it relates with the distribution function of the active centres, the hydrogen species present being affected by the heterogeneity of the surface[1,2]. The situation becomes more intricate if hydrogen not only adsorbs on but also dissolves in the metal, penetrates into the crystal lattice and even changes the crystal parameters.

It is clear that owing to the diverse interactions with the metal, hydrogen can get activated in different ways, and the various hydrogen species that result can exhibit different properties, *e.g.*, in the interaction with organic substances.

Among the most complex is the Pd–H system. Of all metals, palladium exhibits the highest sorption capacity for hydrogen[3]. Sokolskii and Zakumbaeva suggest[4] that dissolved in palladium, hydrogen occurs in the form of protons, the electrons from its atoms occupying sites in the palladium *d* orbitals.

Červený and Růžička published[5] a survey of reactions which give evidence of the protonic nature of hydrogen activated by palladium catalysts; the catalytic activity is shown for the Pd–H system in typical acid catalyzed or acid–base catalyzed reactions (isomerization of olefinic compounds, isomerization of paraffins and cycloparaffins, alcoholysis of oxirane compounds, formation of esters during the hydrogenation of aldehydes and ketones in alcohols, dehydration, decomposition of copper(II) formate in aqueous solution, splitting of hydroxy and ester groups from tertiary

carbon atoms, splitting ether bonds). These reactions take place on palladium catalysts only in the presence of hydrogen, although this presence actually is not required by their stoichiometry.

In the present work, the properties of the Pd–H system are studied on eight palladium catalysts using two test reactions, *viz.* catalytic hydrogenation of cinnamyl methyl ether, which is accompanied by splitting of the C—O bond, and hydrogenation of allylbenzene, which is accompanied by isomerization of the double bond to form a conjugated system with the benzene ring.

EXPERIMENTAL

Chemicals. Cinnamyl methyl ether was prepared by reacting cinnamyl chloride with methanol in alkaline solution[6]; the other chemicals were commercial products: allylbenzene (Soyuzkhim-eksport, Moscow), n-hexane and acetone pure (Lachema, Brno), hydrogen of electrolytical grade (Technoplyn, Prague), palladium dichloride in a 40% solution (Kovohutě, Vestec).

Catalysts. 1 — Pd black prepared conventionally[7], *2* — 5% Pd/CaCO₃ (Koch–Light, U.K.), *3* — 5% Pd/CaCO₃ modified with Pb (Lindlar's catalyst, Farmakon, Olomouc), *4* — 3% Pd/C (Cherox 4100, Chemical Works, Litvínov), *5* — 10% Pd/C prepared as No. 4 using Supersorbon Degussa as support, *6* — 5% Pd/C prepared as No. 4 using graphitized carbon black as support, *7* — 5% Pd/alumina prepared as No. 4 using alumina for commercial Cherox 4000 catalyst (0·56% Pd/Al₂O₃) as support.

Apparatus and procedure. Kinetic measurements were carried out using a conventional apparatus[8] comprising a magnetically stirred glass reactor and a gas burette. Samples for chromatographic analysis were taken periodically. The size of crystallites was measured by the X-ray line broadening (XRLB) method.
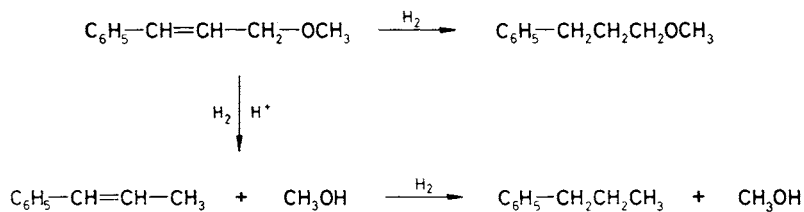
Analytical methods. Gas chromatographic analyses were performed on a Chrom-4 gas chromatograph (Laboratorní přístroje, Prague) with flame ionization detection, using a 2·5 m × 2·5 mm glass column packed with 15% Carbowax 20 M on Chromaton NAW-HMDS. Isothermal measurements were made at 170°C for the hydrogenation of cinnamyl methyl ether and at 140°C for the hydrogenation of allylbenzene.
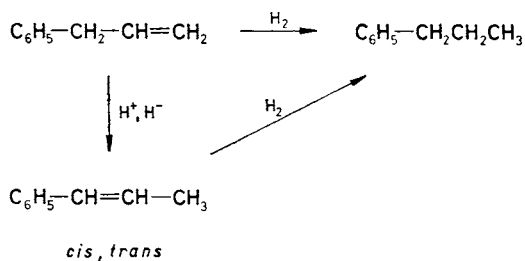
RESULTS AND DISCUSSION

The model reactions were chosen so as to enable not only the hydrogenation activity of the catalysts but also their activity in reactions of different kinds, *viz.* splitting of ether C—O bond (Pathway 1) and isomerization of a double bond to a thermodynamically more stable position (Pathway 2), to be evaluated.

The courses of the two reactions were treated in terms of the time dependences of concentrations of the reaction mixture components. Typical examples are shown in Figs 1 and 2. The initial rates of hydrogen takeup were determined as the slopes of the tangents to the time dependences at time $\tau = 0$. The results are given in Table I along with the selectivities S defined based on the maximum fractions of the side reaction products (propylbenzene for the hydrogenation of cinnamyl methyl ether

(S_1) and 1-phenyl-1-propene isomers for the hydrogenation of allylbenzene (S_2)) in the reaction mixtures.

$$C_6H_5-CH=CH-CH_2-OCH_3 \xrightarrow{\text{H}_2} C_6H_5-CH_2CH_2CH_2OCH_3$$

$$\downarrow \text{H}_2 \mid \text{H}^+$$

$$C_6H_5-CH=CH-CH_3 \ + \ CH_3OH \ \xrightarrow{\text{H}_2} \ C_6H_5-CH_2CH_2CH_3 \ + \ CH_3OH$$

Pathway 1

$$C_6H_5-CH_2-CH=CH_2 \xrightarrow{\text{H}_2} C_6H_5-CH_2CH_2CH_3$$

$$\downarrow \text{H}^+, \text{H}^- \qquad \text{H}_2 \nearrow$$

$$C_6H_5-CH=CH-CH_3$$
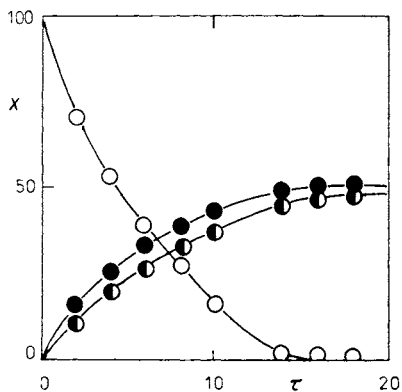
cis, trans

Pathway 2

FIG. 1

Course of hydrogenation of cinnamyl methyl ether in acetone on 10% Pd/C catalyst; x reaction mixture composition (mole %) (solvent not included), τ time (min). ○ Cinnamyl methyl ether, ● 1-phenyl-3-methoxypropane, ◐ propylbenzene
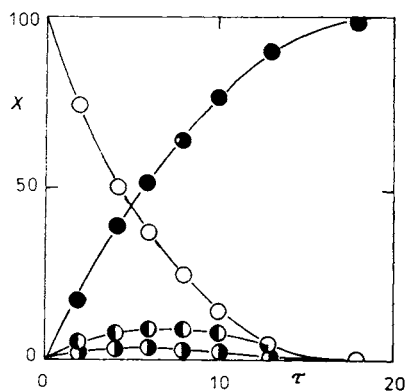

FIG. 2

Course of hydrogenation of allylbenzene in hexane on 5% Pd/γ-alumina catalyst; x and τ as in Fig. 1. ○ Allylbenzene, ● propylbenzene, ◑, ◐ 1-phenyl-1-propene isomers

Hydrogenation of cinnamyl methyl ether was accompanied by splitting of the ether C—O bond giving rise to 1-phenyl-1-propene which was hydrogenated successively to propylbenzene. The saturated 3-phenylpropyl methyl ether did not undergo splitting, which gives evidence that the reactivity of the ether bond is strongly affected by the presence of the double bond. No shift of the double bond to conjugation with the electrons of the ether oxygen (formation of 3-phenylallyl methyl ether) was observed, which is clearly due to the conjugation of the double bond with the benzene ring.

In the hydrogenation of allylbenzene, the route leading to 1-phenyl-1-propene as an intermediate is an intraspheric transfer of hydrogen atoms in the adsorbed state on the catalyst. From the orbital theory standpoint this hydrogen transfer is conceivable both *via* the proton and the hydride forms[9-11], although the latter should proceed more easily.

The activities of the catalysts in the two hydrogenation reactions were compared with the size of the crystallites as determined by the X-ray diffraction method, and no correlation between them was disclosed. Since the true surface area of the active component of the catalyst could not be determined by any other independent method, it is hard to assess to what extent the true size of crystallites, and thus the surface area of the active metal, is accounted for by the nonuniform morphological shape of the palladium crystallites on the different supports and to what extent the hydrogenation rates are affected by the catalytic effect of the support. At any rate, it is clear that the X-ray method does not suit to the determination of the surface area of the active metal on different supports.

The data in Table I demonstrate that the hydrogenation reactivity is higher for allylbenzene than for cinnamyl methyl ether in both solvents and on all of the catalysts tested. An approximately linear relationship exists between the reaction rates of the two substances in the two solvents and on the catalysts used.

The hydrogenation rates on Pd black are about $3-4\cdot5$ times lower in acetone than in hexane; on the remaining catalysts the rates in the two solvents do not differ so much. (Hydrogenation of cinnamyl methyl ether on Lindlar's catalyst, $Pd-Pb/CaCO_3$, is a special case, this catalyst having an exceptional position owing to the presence of the modifying lead.) The above effect is probably associated with the aggregation of particles on the palladium black, which has been observed in the polar acetone.

The selectivities are more complicated to evaluate. No relation was found between the selectivities of the two test reactions, whether for one reaction in the two solvents or for the two reactions always in the same solvent. For the hydrogenation of cinnamyl methyl ether in hexane, the selectivity was highest on Pd black and nil on 5% Pd/ /$CaCO_3$ and 5% Pd/alumina, whereas for the remaining catalysts the selectivities did not differ substantially. The discrimination was somewhat more pronounced in the palladium-to-support surface area ratio based on experience. This ratio can be expected to decrease in the catalyst series $1 \geqq 6 > 8 > 5 > 2 \geqq 7 \sim 4 \gg 3$.

TABLE I
Kinetic data of the model reactions

No.	Catalyst	Pd crystallite size, nm	Hydrogenation of cinnamyl methyl ether[a]						Hydrogenation of allylbenzene[a]					
			hexane		acetone		R_{rel}	S_{rel}	hexane		acetone		R_{rel}	S_{rel}
			R_{1H}	S_{1H}	R_{1A}	S_{1A}			R_{2H}	S_{2H}	R_{2A}	S_{2A}		
1	Pd black	17·3	29·3	16·8	6·4	52·9	4·5	0·32	48·8	22·0	15·2	14·5	3·0	1·52
2	5% Pd/CaCO$_3$	11·3	147·0	0·0	107·7	21·1	1·4	0·00	283·4	9·6	9·6	175·5	1·6	0·79
3	5% Pd–Pb/CaCO$_3$	—	22·2	5·5	2·9	—[b]	7·6	—	32·9	8·0	40·3	9·1	0·8	0·88
4	3% Pd/C–Degussa	11·3	49·1	5·9	62·4	37·5	0·8	0·16	127·0	8·2	127·7	15·6	1·0	0·53
5	10% Pd/C–Degussa	49·0	78·6	6·8	104·8	48·9	0·8	0·14	152·8	16·9	166·9	18·4	0·9	0·92
6	5% Pd/carbon black	9·2	37·7	6·7	33·5	57·2	1·1	0·12	73·0	25·5	74·9	25·3	1·0	1·01
7	5% Pd/alumina	32·6	225·2	0·0	175·7	41·1	1·3	0·00	424·6	11·9	314·7	12·9	1·3	0·92
8	10% Pd/BaSO$_4$	9·8	159·2	6·4	122·0	51·4	1·3	0·12	229·7	19·7	142·2	14·8	1·6	1·33

[a] R initial rate of conversion of the starting substance expressed based on the hydrogen takeup (mmol H_2/min g_{Pd}), S selectivity expressed as the maximum propylbenzene or 1-phenyl-1-propene content (mol.%) with respect to the starting substance), R_{rel} ratio of the initial reaction rates (R) in hexane and acetone, S_{rel} ratio of selectivities (S) in hexane and acetone; [b] reaction was not conducted to the total conversion of the starting substance.

The selectivity of hydrogenation of cinnamyl methyl ether increased markedly when passing from hexane to acetone (Table I). Taking into account the possibility that during its adsorption on the catalyst surface, hydrogen can split up and interact with solvent, following, for instance, the pathway

$$M + H_2 \rightarrow 2(MH_{ad}) + Sol \rightarrow MH^- + H^+ Sol$$

as discussed by Dorfman[11], it can be assumed that this reaction will occur to a greater extent in the polar acetone, where the possibility of stabilization of the proton by solvation is considerably higher than in the nonpolar hexane. The readiness of splitting of the ether bond is promoted by the adsorption of the cinnamyl methyl ether molecule and by the conjugation of the double bond with the benzene ring, which undoubtely alters the electronic structure of the adsorbed ether. The splitting of the ether bond then can be due to the effect of either hydride hydrogen or proton in $H^+ Sol$, the latter being more likely (compare, *e.g.*, with the Zeiss cleavage of ethers).

In the hydrogenation of allylbenzene, the effect of solvent on the selectivity is much less marked, which suggests that the charge of the adsorbed hydrogen plays nearly no role in the isomerization reaction. The selectivities, particularly S_{2H}, demonstrate that the isomerization ability increases with increasing palladium-to-support surface area ratio (see above), hence in the direction where the properties of palladium metal become increasingly apparent. The amount of the isomers (1-phenyl-1-propene) forming during the hydrogenation of allylbenzene is clearly dependent on the frequency of the adsorption-desorption processes of the two substances. The nonzero S_2 values also document that the rate of intramolecular displacements of hydrogen is higher than the rate of the hydrogenation reaction itself.

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