Liquid phase hydrogenolysis of dibenzyl ether over metals of the VIIIth group

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It has been shown that depending on the catalyst and the solvent used, during the conversion of dibenzyl ether to toluene hydrogenolysis of C—O ether bonds, dehydrogenation and hydrogenolysis of benzyl alcohol formed, hydrogenation and decarbonylation of benzaldehyde, and the recombination of benzyl radicals and the benzylation of toluene can take place. The activity of catalysts in hydrogenolysis reactions of dibenzyl ether and benzyl alcohol to produce toluene decreases as follows: Pd/C > Pd > Raney Ni > Rh, whereas the selectivity drops down in the order: Raney Ni > Pd > Pd/C > Rh. The reaction rates depend on the solvent and diminish in the order: ethanol > 2-propanol > benzene.

Key words: hydrogenolysis, hydrogenation, dibenzyl ether, group VIII metals as catalysts.

The hydrogenolysis of benzyl ether C—O bond proceeds in the presence of metals of the VIIIth group under mild conditions and is routinely used for elimination of the benzyl protective group in organic syntheses.[1] The conversion of dibenzyl ether to toluene has been studied previously in the presence of $ZnCl_2$ with Ni, Mg, and Zn additives, but the mechanism of the reaction was not considered.[2] The purpose of the present paper is to study the mechanism of hydrogenolysis of dibenzyl ether and the effect of the catalyst, the solvent used, and the composition of the gas phase (H_2 and Ar) on the process.

Experimental

Metal blacks as catalysts were prepared by the reaction of Pd, Rh, or Ru chlorides with $NaBH_4$, and 2 % Pd/C was prepared by the impregnation method.[3] Raney Ni was obtained by leaching a Ni—Al alloy (1:1) with a 25 % aqueous NaOH solution at 96° C for 2 h.

The purities of dibenzyl ether, benzyl alcohol, and benzaldehyde were at least 98 % according to GLC.

The experiments were performed in a thermostatted reactor under static conditions at 70° C, ambient pressure (H_2 or Ar) and intense shaking (more than 300 shakes per min) ensuring the kinetic regime of the reaction. The starting compound (5 mmol), the solvent (20 ml) and the catalyst (2 % Pd/C or Raney Ni in an equal amount by weight of the substrate, and Pd, Rh, and Ru blacks in 20 % of the weight of the substrate) were mixed in a reactor. The products were analyzed by GLC with a LKhM-8MD chromatograph equipped with a flame ionization detector and a column (2 m × 3 mm) packed with 15 % Tritone 505 on Celite X-545. In GLC analyses a temperature program (35°C — 190°C at 20 °C min^{-1}) was used. *o*-, *m*-, and *p*-Benzyltoluenes and dibenzyl were identified with a Finnigan MAT, Incar 50 GLC—MS instrument, equipped with a RSL-20 column (30 m length). The catalytic activities were estimated by the ratio of the initial rates of hydrogenolysis of dibenzyl ether ($w_{0,\text{eth}}$) and benzyl alcohol ($w_{0,\text{alc}}$) to the mass of the catalyst. The catalytic activities were also characterized by the ratio $w_{0,\text{eth}}(\text{alc})/w_{0,\text{st}}$ where $w_{0,\text{st}}$ is the initial rate of hydrogenation of the C=C bond of styrene under identical conditions.

Results and Discussion

In the presence of Pd, Ni, and Rh catalysts in an H_2 atmosphere dibenzyl ether undergoes hydrogenolysis of the C—O bonds to form toluene in a 51—92 % yield (Table 1).

The reaction rate depends on the metal and varies over a wide range. Thus, the initial rate of hydrogenolysis of the ether on a Pd/C catalyst is ~300 times higher than that on Rh black (23.5 and 0.08 mmole (min g(met))$^{-1}$ resp.), while the values of the relative activities ($w_{\text{eth}}/w_{\text{alc}}$), which make it possible to exclude the effect of dispersity, porosity, etc. are 0.48 and 0.01 respectively. The activities of catalysts in dibenzyl ether hydrogenolysis increase as follows: Rh < Raney Ni < Pd < Pd/C.

The shape of the kinetic curves on Fig. 1 shows that dibenzyl ether transforms into toluene and benzyl alcohol. The latter also undergoes hydrogenolysis to form toluene. In the presence of Pd/C even at the early stages of the conversion of the ether the amount of toluene is about 5 times greater than that of benzyl alcohol.

It can be assumed that the conversion of dibenzyl ether to toluene proceeds both as two-step and direct transformations without desorption of benzyl alcohol.

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Table 1. The effects of catalysts and solvents on transformations of dibenzyl ether, benzyl alcohol, and benzaldehyde in a H_2 atmosphere

Catalyst	Solvent	Compound	Time/h	Degree of conversion (%)	Yield (%)			w_o*, $\frac{\text{mmol}}{\text{min} \cdot \text{g(M)}}$**	$w_{o,rel}$***
					$PhCH_3$	$PhCH_2OH$ (max)	Dibenzyl + benzyltoluenes (max)		
Pd/C	Ethanol	$(PhCH_2)_2O$	2.0	98.2	96.7	9.1	2.9	42.20[a]	—[d]
	2-Propanol		4.0	97.0	95.2	10.4	3.1	23.5[a]	0.48[d]
	Benzene		2.0	30.0	17.3	13.9	7.0	1.08[a]	—[d]
Pd	2-Propanol		5.0	96.0	90.8	16.1	2.9	1.00[a]	0.32[d]
Raney Ni	—		12.0	94.6	92.1	20.6	1.9	0.08[a]	0.12[d]
Rh	—		12.0	70.2	51.2	16.5	6.7	0.08[a]	0.01[d]
Pd/C	Ethanol	PhCHO	0.6	97.6	97.6	3.3	—	228.5[b]	—[e]
	2-Propanol		0.3	98.2	97.2	13.3	—	110.2[b]	2.91[e]
	Benzene		3.0	20.2	5.0	14.2	—	1.56[b]	—[e]
Pd	2-Propanol		—	—	—	—	—	—[b]	2.6[e]
Raney Ni	—		—	—	—	—	—	—[b]	1.6[e]
Rh	—		—	—	—	—	—	—[b]	2.0[e]
						PhCHO			
Pd/C	Ethanol	$PhCH_2OH$	0.3	99.9	99.9	60.3	—	132.09[c]	—[f]
	2-Propanol		1.5	80.0	75.5	39.0	—	64.44[c]	1.42[f]
	Benzene		4.0	90.4	80.0	27.0	—	31.86[c]	—[f]
Pd	2-Propanol		4.5	54.1	52.2	11.0	—	2.59[c]	0.81[f]
Raney Ni	—		6.0	68.8	66.9	Traces	—	0.13[c]	0.20[f]
Rh	—		9.0	29.2	29.2	—	—	0.16[c]	0.02[f]

* w_0 is the initial rate of hydrogenation for: [a] dibenzyl ether; [b] benzaldehyde (70 °C, 1 atm of H_2); [c] benzyl alcohol.

** M is metal.

*** $w_{0,rel}$ is the ratio between the initial rates of hydrogenation: [d] $w_{0,eth}/w_{0,st}$; [e] $w_{0,alc}/w_{0,st}$; [f] $w_{0,alc}/w_{0,eth}$.

At the early stage of hydrogenation in the presence of Raney Ni and Rh black the molar ratio toluene : benzyl alcohol is stoichiometric (when the conversion of dibenzyl ether is less than 20 %). It is noteworthy that small amounts of *o*-, *m*-, and *p*-benzyltoluenes and dibenzyl (1.9—6.7 %) are found in the reaction products. These substances are presumably formed through the alkylation of toluene and the recombination of benzyl radicals (Table 1). The formation of 2—4 % benzaldehyde is observed in the presence of Pd catalysts (Fig. 1, *a*).

The initial rates of hydrogenolysis of benzyl alcohol are 1.6—2.9 times higher than those of dibenzyl ether,

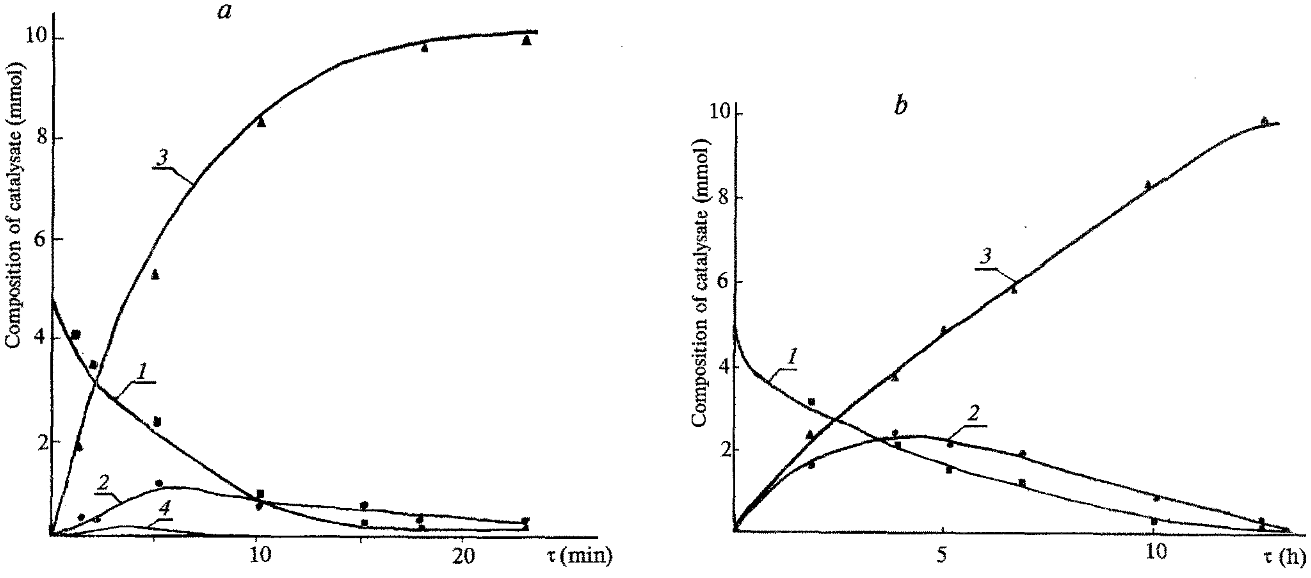


Fig. 1. Hydrogenolysis of dibenzyl ether in the presence of Pd/C (*a*) or Raney Ni (*b*): dibenzyl ether (*1*); benzyl alcohol (*2*); toluene (*3*); benzaldehyde (*4*) (70 °C, 1 atm of H_2).

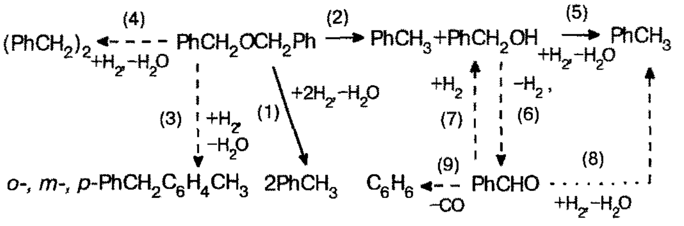
whereas the order of activities is the same. In contrast to Raney Ni and Rh black, in the presence of Pd catalysts the formation of benzaldehyde (39 % yield) is observed at the early stage of hydrogenolysis; then the benzaldehyde is reduced or partially decarbonylated to form benzene (2–4 %). It seems unlikely that benzyl alcohol would yield benzaldehyde under hydrogenation conditions, though it is known that at high temperatures in the presence of Pd or Raney Ni and in the absence of H_2 the disproportionation reaction of benzyl alcohol proceeds with the formation of benzaldehyde, toluene, and water.[4]

It is noteworthy that the yield of benzaldehyde in the hydrogenation of benzyl alcohol depends on the amount of the catalyst (Pd/C). When the amount of catalyst is doubled (from 0.54 to 1.08 g) the maximum yield of benzaldehyde achieves 46 %, while the yield does not exceed 4 %, when a smaller amount (0.054 g) of the catalyst is used.

The transformation of benzaldehyde to toluene on Pd/C in 2-propanol proceeds at a high rate, and the formation of benzyl alcohol is quite low (13.3 %, see Table 1). Taking this fact into account and comparing the rates of conversion of benzaldehyde (110 mmole $(\text{min g of Pd}))^{-1}$ and benzyl alcohol (69 mmole $(\text{min g of Pd}))^{-1}$ it can be hypothesized that the conversion of benzaldehyde to toluene may occur either through intermediate formation of benzyl alcohol or through direct hydrogenation of the carbonyl group. The straightforward reduction of the C=O group has been previously proposed for the hydrogenation of cyclohexanediones on Pt (see Ref. 5) and acetylbutyrolactone on Pd/C, Pt/C, and Rh/C (see Ref. 6).

Thus, the catalytic conversion of dibenzyl ether can be represented as follows (Scheme 1):

Scheme 1



All these routes occur on Pd and Pd/C: dibenzyl ether undergoes hydrogenolysis with the formation of toluene (reaction 1), or toluene and benzyl alcohol (reaction 2), the latter is then reduced to toluene (reaction 5) or partially dehydrogenated to benzaldehyde (reaction 6). The latter is transformed to toluene *via* the intermediate formation of benzyl alcohol (reactions 5, 7) or directly (reaction 8). Some side reactions also take place: decarbonylation of benzaldehyde to benzene (reaction 9), alkylation of toluene with the formation of *o*-, *m*-, and *p*-benzyltoluenes (reaction 3), and recombination of benzyl radicals to form dibenzyl (reaction 4).

In the presence of Raney Ni and Rh the conversion of dibenzyl ether proceeds on pathways 1–5 without benzaldehyde formation. The selectivity of toluene formation on Raney Ni is higher than that on Pd, since benzene is absent from the reaction products, and the yields of benzyltoluenes and dibenzyl are lower (Table 1), whereas in the presence of Rh the selectivity of toluene formation is low as the result of the greater contribution of reactions 3 and 4. So, the order of catalyst selectivity during dibenzyl ether hydrogenolysis in relation to toluene formation is as follows: Raney Ni > Pd > Pd/C > Rh. In the presence of Ru the hydrogenolysis of dibenzyl ether and benzyl alcohol does not take place under the conditions studied.

The nature of the solvent used also has a substantial effect on the transformations of $(PhCH_2)_2O$, $PhCH_2OH$ and PhCHO (Table 1). The Pd/C-catalyzed reactions proceed at a high rate and with a high yield of toluene in ethanol and 2-propanol. At the early stage of the hydrogenation of benzyl alcohol a large amount of benzaldehyde is formed (up to 60 % in ethanol). The rate of the reaction is decreased in benzene and the selectivity of the formation of toluene in hydrogenolysis of dibenzyl ether is also decreased as the result of the formation of isomeric benzyltoluenes and dibenzyl. In addition, alkylation with the formation of diphenylmethane in 1–2 % yield is observed under these conditions. The reduction of PhCHO is especially sensitive to the nature of the solvent. Thus, the initial rate of hydrogenation of benzaldehyde in benzene is 146 times lower than in ethanol, whereas in the case of benzyl alcohol the rates differs only by a factor of four (Table 1).

In an inert atmosphere (Ar) dibenzyl ether and benzaldehyde do not undergo transformations on the catalysts studied, but benzyl alcohol affords benzaldehyde, toluene, and water (on Pd), or benzaldehyde (on Ru), or toluene (on Raney Ni) (Table 2). In the latter case, the reaction evidently proceeds as hydrogen transfer from 2-propanol; the presence of acetone among the reaction products confirms this assumption. Benzyl alcohol remains unchanged in the presence of Rh.

In the presence of Pd/C or Pd black in an Ar atmosphere benzyl alcohol smoothly affords benzaldehyde and toluene. The rate of the reaction depends on the solvent and increases as follows: $C_6H_6 <$ < 2-propanol+H_2O < 2-propanol < EtOH (Table 2). The distribution of the products of benzyl alcohol disproportionation do not coincide with calculations: the yield of benzaldehyde exceeds the yield of toluene (Fig.2).

Previously it was shown[7] that benzyl alcohol can be used as a source of hydrogen for the selective reduction of unsaturated steroids in the presence of Pd/C; if an effective hydrogen acceptor is absent, benzyl alcohol behaves as both a donor and an acceptor of hydrogen. So, in the presence of Pd/C disproportionation of benzyl alcohol probably does not take place; rather dehydrogenation is followed by hydrogenolysis to form ben-

Table 2. The effects of catalysts and solvents on transformations of benzyl alcohol (Ar, 70°C)

Catalyst	Solvent	Time/h	Initial rate	Degree of conversion (%)	Yields (%)	
					$PhCH_3$	PhCHO
Pd/C	Ethanol	6.5	5.14	55.5	16.5	39.1
	2-Propanol	9.0	3.09	64.8	20.9	43.9
	2-Propanol + H_2O (1:1)	19.0	2.56	31.0	6.1	24.5
	Benzene	14.0	0.93	35.7	2.9	32.8
Pd	2-Propanol	5.0	0.17	11.4	4.2	7.2
Raney Ni	—	15.0	0.014	25.5	15.5	—
Ru	—	16.0	0.03	19.8	—	19.8

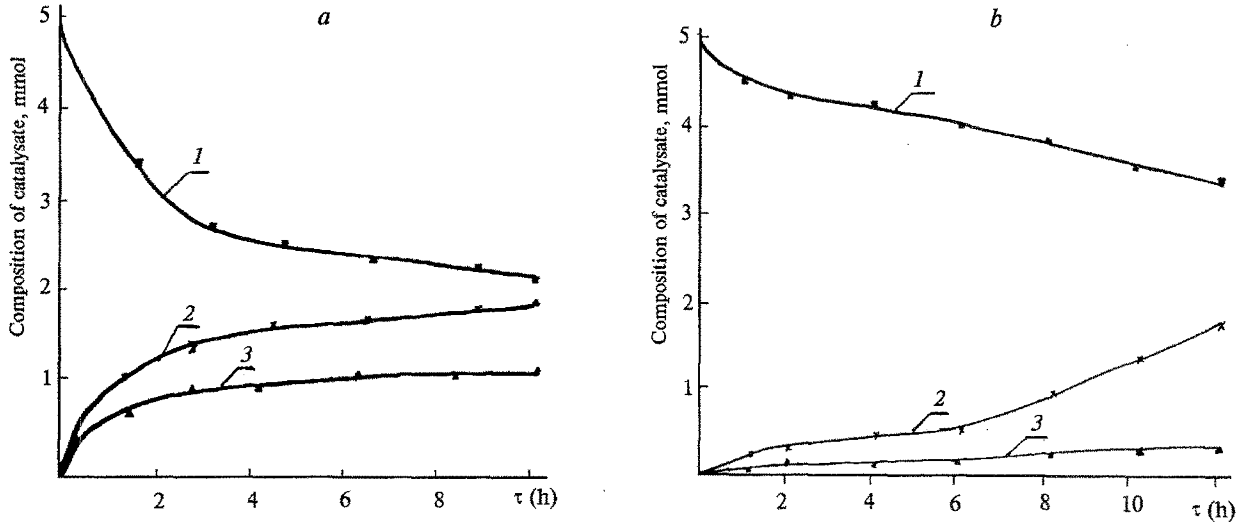


Fig. 2. Conversion of benzyl alcohol under Ar on Pd/C, using ethanol (*a*) or benzene (*b*) as the solvent: benzyl alcohol (*1*), benzaldehyde (*2*), toluene (*3*).

zaldehyde and toluene respectively. As the conversion of benzyl alcohol increases, the contribution of the second reaction decreases, hence the toluene concentration increases more slowly (Fig.2). This can be explained by the inhibition of hydrogenolysis due to co-adsorption of the reaction products, *i.e.*, benzaldehyde, toluene, and water.[8]

When the reaction is carried out in benzene, a decrease both in the rate of conversion and in the contribution of hydrogenolysis *vs.* dehydrogenation is observed. The probable reason for this fact is adsorption of the solvent on the surface of the catalyst.

It is known[1,2] that Lewis acids promote hydrogenolysis of the C—O bond. Indeed, the addition of a small amount of $ZnCl_2$ (Pd/C, 2-propanol, Ar) increased the total rate of conversion and changed the ratio of the reaction products in favor of toluene. The above observation also confirms the assumption that in the presence of Pd catalysts, hydrogenolysis and dehydrogenation proceed simultaneously.

Therefore, the conversion of dibenzyl ether over metals of VIIIth group is a complex multichannel process, which can include hydrogenolysis of the C—O bond of the ether, dehydrogenation and hydrogenation of benzyl alcohol and benzaldehyde formed, recombination of benzyl radicals, alkylation of toluene, and decarbonylation of benzaldehyde, depending on the nature of the solvent and the catalyst.

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