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Reactions of Primary and Secondary Alcohols over Palladium–Cab-O-Sil Catalysts in the Presence of Hydrogen: Variables Affecting Ether Formation

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Palladium oxide on Cab-O-Sil (10% Pd) reduced at 300°C was found to be an effective catalyst for the conversion of primary alkanols to the corresponding ethers. The reaction was carried out in a flow type microreactor attached to a gas chromatograph through which a molar ratio of 3.1 to 1.0 of hydrogen and alcohol were passed. The selectivity toward ether formation at 160°C was of the order of about 93% in the case of 1-propanol and 1-butanol. The yield of dineopentyl ether under similar conditions amounted to 73%.

Secondary alkanols produced both ethers and alkanes, the relative amounts depending on the temperature to a very pronounced degree. Thus the amount of diisopropyl ether obtained from 2-propanol dropped from 52 mol% to 3.5 when the temperature was raised from 160 to 190°C. This behavior could be correlated with the influence of Pd-catalyst on diisopropyl ether and di-*n*-butyl ether at 190°C. While the former decomposes entirely, the latter remains virtually unaffected.

The substitution of hydrogen by helium reduces the total conversion to about 20%. This occurs at the expense of ether formation. On the other hand, a drop in the activity of the Pd-catalysts results if the catalyst is left to cool in a current of hydrogen. This effect is reversed on heating. It thus seems that it is connected with adsorption of hydrogen on the active sites, which is in accord with the particular chemistry of Pd and hydrogen.

Injection of air increases the selectivity toward ether, e.g., to 89% in diisopropyl ether formation at 160°C. This effect is explained by the formation of new basic sites. It is reversed by subsequent treatment in a current of hydrogen.

INTRODUCTION

In a previous study of the reactions of alcohols over transition metal catalysts it was reported that over reduced nickel oxide and in the presence of a flow of hydrogen primary alcohols and to a somewhat smaller extent secondary alcohols were converted at 160 to 190°C to the corresponding ethers (*1*). Using nickel as catalyst and a pulse reactor, the selectivity of conversion of *n*-butanol to di-*n*-butyl ether was over 90%. Under similar experimental conditions reduced non-supported palladium oxide gave 66% selectivity, iridium, 78%; rhodium, 37%; and platinum showed no conversion of primary alcohols to ethers.

A more detailed study of the effect of palladium as catalyst for the formation of ethers from primary and secondary alcohols is being described using a flow microreactor and reduced palladium oxide–Cab-O-Sil catalyst. Cab-O-Sil which is a commercial calcined silica and which is per se catalytically inert, was found previously to be an effective support for nickel.

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PREPARATION OF CATALYST

The starting material was either palladium(II) chloride or nitrate. The salts on exposure to moist air undergo hydrolysis to the insoluble hydrated oxides. The oxides were reduced by a current of hydrogen at room temperature and followed by a current of helium.

The hydrogen-free palladium was readily dissolved in concentrated nitric acid and the solution was diluted 10-fold or more with water. The nitric acid solution was then electrolyzed, whereby the palladium metal was being deposited at the platinum screen cathode. The voltage was kept sufficiently low to prevent hydrogen evolution which would make the palladium sensitive to oxidation. The cathode was washed with water, followed with acetone, and weighed. The palladium was then dissolved in concentrated nitric acid, and the cathode was weighed again. The difference in coated and uncoated cathode was the weight of palladium in the nitric acid solution. Additional concentrated nitric acid was added to the palladium solution, up to the neck of the volumetric flask. This solution was stored and samples of known amounts of palladium were pipeted out from it.

Supported palladium catalysts were prepared by the following procedure. The nitric acid solution was condensed at ambient temperature under reduced pressure to the point where a sticky mass began to form. This mass was dissolved in water and heated until the color changed from yellow or bright brown to deep-brown. The solution was then cooled, the support added, and several drops of aqueous ammonia were introduced while the mixture was stirred. Addition of a large amount of ammonia leaves part of the palladium in solution. After a few minutes of stirring the mixture was filtered, and the product was washed with water and dried. The temperature of drying should not be much above 100°C. At higher temperature a gray-brown powder is obtained, which after reduction produces a catalyst of poor activity. At low temperature of drying the powder is brown and after reduction shows a high catalytic activity.

The support was Cab-O-Sil M-5 (Cabot Corp., Boston, Mass.) which is a calcined silica in the form of fine powder. The catalyst cake which was obtained from the impregnated palladium salt was dried and crushed to 100 to 200 mesh powder. The latter was reduced with hydrogen, according to the previously described procedure (*2*, *3*). Cab-O-Sil per se does not possess catalytic activity (*3*, *4*).

The final catalyst was composed of 10% by wt of Pd on Cab-O-Sil.

EXPERIMENTAL CONDITIONS AND RESULTS

The experiments were made in a flow-type microreactor attached to a gas chromatograph (*2*, *7*). In each experiment about 200 mg of a 100 to 200 mesh catalyst was used. "Standard conditions" were used throughout unless indicated otherwise and which consisted of passage of 11.8 ml hydrogen/min with a molar ratio of hydrogen to alcohol equal to 3.1 to 1.0.

The gaseous and liquid products were analyzed by gas chromatography, according to the procedure described previously (*2*, *7*, *8*).

Effect of temperature of reduction of the catalyst. It was reported previously that in the conversion of alcohols to ethers over reduced nickel oxide the temperature of reduction of the oxide has an important effect upon the activity and selectivity of the catalyst (*1*, *3*, *6*). The present study of the reduction of 10% palladium on Cab-O-Sil has likewise revealed that the temperature of reduction has an effect upon the conversion of alcohols to ethers and that the optimal temperature is in the range of about 300 vs 400 to 450°C for 7% Ni–Cab-O-Sil catalyst, Table 1.

The length of reduction also influences

TABLE 1

Effect of Temperature of Reduction on Reactions of Alcohols at 160°C[a]

Alcohol	Reduction temp (°C)	Time (hr)	Conversion (%)	Product (%)[b]		
				Ether	C_3H_8	C_2H_6
2-Propanol	190	2	9.4	71.6	28.4	—
	190	14	31	32.3	67.7	—
	190	72	38	29.3	70.7	—
	250	—	40	40	60	—
	300	14	55	52.7	47.3	—
	350	14	50	50	50	—
	400	14	40	45	55	—
1-Propanol	190	14	8.7	95.3	4.7	Tr
	250	14	11.1	95.5	4.5	Tr
	300	14	13.2	95.4	4.6	Tr
	350	14	12.4	92.7	6.4	0.8
	400	14	11.8	93.2	5.1	1.7

[a] Amount of catalyst, 200 mg; H_2 flow rate, 11.3 ml/min.

[b] On acetone or aldehyde free basis. Equilibrium concentration of acetone is obtained in each experiment. Only a small amount of aldehyde, less than 1% is present.

the activity of the catalysts. At a reduction temperature of 190°C, after 2 hr of reduction only 9.4% of 2-propanol underwent conversion, on acetone free basis, at 160°C, with 71.6% selectivity towards ether formation. With about 14 hr reduction the total conversion of the alcohol increased to 31%, but the selectivity dropped to 32.3%. The extension of the time of reduction to 72 hr had a relatively small effect both upon the conversion and selectivity of the reaction.

It is of interest to note that after the catalyst was reduced for 72 hr at 190°C and it was cooled overnight to room temperature in a current of hydrogen, its activity towards dehydration of 2-propanol dropped almost completely, however, this catalyst was still active toward dehydrogenation. An equilibrium concentration, 16% of acetone, was present in the product. This phenomenon was also observed when the catalyst was cooled from 250°C to room temperature in the presence of hydrogen. The catalyst was restored, however, to its original activity through a series of reductions and passages of alcohol over the catalyst at 190°C. Cooling in a current of helium, or leaving the catalyst overnight in a current of helium at 190°C caused no change in its activity.

Reaction of Alcohols and Ethers

Both primary and secondary alcohols were passed over 10% Pd on Cab-O-Sil which was reduced at 300°C for about 14 hr. The experiments were made at 160 and 190°C using molar ratio of hydrogen to alcohols equal to 3.1 to 1.0, Table 2.

At 160°C 1-propanol and 1-butanol yielded 95.4 and 91.9% of ethers, respectively, with a conversion of over 13%. At 190°C the selectivity to ether dropped to 86% with conversion of the alcohols doubling. At the higher temperature part of the 1-butanol undergoes reductive dehydroxymethylation with accompanying formation of propane. In the case of 1-propanol the main side product was the formation of propane as a consequence of dehydration of 1-propanol followed by hydrogenation of the olefin. A similar type of reaction occurs when 2,2-dimethylpropanol (neopentyl alcohol) is passed over palladium–Cab-O-Sil. Dineopentyl ether was the major product at 160°C, and isopentane, resulting from the dehydration followed by hydrogenation, was the main product from the experiment made at 190°C.

Hydrogen, as it was already shown in the case of nickel on Cab-O-Sil catalyst, is an integral part of the catalytic system (*9*). When 1-butanol was passed over Pd on Cab-O-Sil in a flow of helium, both the conversion and the yield of ether produced dropped considerably and reductive dehydroxymethylation accompanied by formation of propane became an essential part of the reaction.

2-Propanol, being a secondary alcohol, is more sensitive to the action of Pd–SiO_2 catalyst; at 160°C the conversion of the carbinol was 55% and at 190°C it was 85%, the ether yields were 52 and 3.5%, respectively. Propane was the main product of reaction at 190°C. 2-Butanol and 2-pentanol afforded at 160°C 34.5 and 19.4% of the corresponding ethers, and again the reductive dehydration was the main reaction.

Di-*n*-butyl ether is resistant to the action of Pd/Cab-O-Sil at 190°C. Over 99% of the ether was recovered, which is in agreement with the results obtained with Ni/Cab-O-Sil (*9*). Diisopropyl ether on the other hand undergoes reaction when passed over the palladium catalyst forming propane as the major product, 72.8%, and 2-propanol as the minor product. According to stoichiometry part of the propane must have been produced from 2-propanol generated from the hydrogenolysis of ether.

TABLE 2

Conversion of Alcohols and Ethers over Palladium–Cab-O-Sil Catalyst[a]

Expt	Reactant	Temp (°C)	Carrier gas	Conversion	Product (mol%)				
					Ether	C_2H_6	C_3H_8	C_4H_{10}	Miscellaneous
1	1-Propanol	160	H_2	13.2	95.4	Tr	4.6	—	—
		190	H_2	24.1	86.3	1.6	12.9	—	—
2	1-Butanol	160	H_2	14.2	91.4	—	2.1	6.0	—
		190	H_2	25.8	85.7	—	10.8	3.5	
3	1-Butanol	160	He	2.9	64	—	24	12	—
		190	He	5.8	35.7	—	32.2	32.1	—
4	2,2-Dimethylpropanol[b]	160	H_2	6.7	73.4	—	—	—	26.6[c]
		190	H_2	19.9	33.2	—	—	—	66.8[c]
5	2-Propanol	160	H_2	55	52	—	48	—	
		190	H_2	85	3.5	—	96.5	—	
6	2-Butanol	160	H_2	58	34.5	—	—	65.5	—
7	2-Pentanol	160	H_2	62	19.4	—	—	—	80.6[d]
8	Di-*n*-butyl ether	190	H_2	~1					
9	Diisopropyl ether	190	H_2	31.6	—	—	72.8	—	27.2[e]

[a] Experimental conditions as in Table 1, footnote *a*; the catalyst was reduced at 300°C for 14 hr.

[b] The alcohol was dissolved in equal weight of *n*-heptane.

[c] Isopentane.

[d] *n*-Pentane.

[e] 2-Propanol.

TABLE 3

Passage of Binary Mixtures of Alcohols over Pd–Cab-O-Sil at 160°C[a]

Reactants[b] I = 2-C_3H_7OH II =	Molal ratio H_2/ I + II	Conversion (%)		Composition of product, based on I and II (mol%)						
		I	II	Symmetrical ethers		Mixed ethers		C_3H_8 I	n-C_4H_{10} II	n-C_5H_{12} II
				I	II	I	II			
1-C_4H_9OH	2.1	12.0	2	18.2	50.0	9.1	50.0	72.7	—	—
1-C_4H_9OH	2.5	22.5	4.5	21.6	44.4	13.5	55.6	64.9	—	—
1-C_4H_9OH	3.1	37	12	32.3	45.4	19.3	54.6	48.4	—	—
1-C_4H_9OH	4.1	40	10	28.6	40	17.5	55	53.9	5	—
2-C_4H_9OH	3.1	24.5	33.5	30	32.8	19	13.4	51	53.8	—
2-$C_5H_{11}OH$	3.1	18	31	22.2	25.8	16.7	9.7	61.1	—	64.5

[a] Effect of ratio of hydrogen to alcohols. Conditions same as Tables 1 and 2, footnote *a*, unless indicated otherwise.

[b] Equimolar mixtures of I and II were used in each experiment.

As with nickel the ratio of hydrocarbons to ethers formed from secondary alcohols is increased as the alkyl group is lengthened (*10*). However, in the case of nickel there is an appreciable difference toward ether formation between 2-propanol and 2-butanol but no such difference was observed between 2-butanol and 2-pentanol, and this was attributed to steric effects. In the case of Pd–Cab-O-Sil catalyst the difference in the amount of ether formed is also significant between 2-butanol and 2-pentanol. Inasmuch as these two alcohols are almost equivalent sterically, E_s being -1.13 and -1.12, respectively, the difference in ether formation is attributed to polarity of the two alcohols σ^* for 2-butanol being -0.210 and for 2-pentanol, -0.220 (*11*). It can thus be assumed that polar catalytic sites in Pd–Cab-O-Sil play a more important role than in Ni–Cab-O-Sil.

Reactions of Mixtures of Alcohols

Equimolar mixtures of two alcohols were passed over Pd–Cab-O-Sil in order to determine the effect of structure of the alcohols upon the formation of symmetrical and mixed ethers.

A mixture of two secondary alcohols yielded an equimolar ratio of symmetrical ethers with a total yield of 63 in the case of 2-propanol and 2-butanol and 48% in the case of 2-propanol and 2-pentanol, respectively. The contribution of 2-propanol to the formation of mixed ether was higher than that of its homologues, 19 vs 13.4%, and 16.7 vs 9.7 in the case of 2-butanol and 2-pentanol, respectively, Table 3.

In the case of an equimolar mixture of 2-propanol with 1-butanol, the latter showed a low conversion with 50% selectivity to form symmetrical and 50% to mixed ethers. The yield of symmetrical ether produced from 2-propanol was 18.2% and of mixed ether, 9.1, accompanied by the formation of 72.7% of propane.

When the molar ratio of hydrogen to the equimolar mixture of 2-propanol and 1-butanol passed over the catalyst was increased from 2.1 to 2.5, 3.1, and 4.1, the conversion of the alcohols increased progressively from 14 to 50%. A more detailed study of this observation is contemplated.

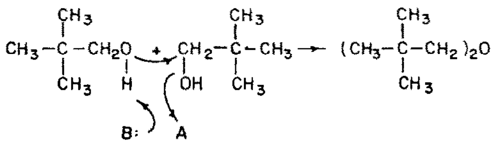
Effect of Injection of Air

The injection of 50 ml of air over 200 mg of Pd–Cab-O-Sil caused a pronounced increase in the selectivity of the conversion of 2-propanol to ether, with simultaneous decrease in overall initial activity of the catalyst, Table 4. In the course of time the effect of air was slowly diminished and after 6 hr on run the original activity of the catalyst was almost restored. The reproducibility of the reaction is very good. The effect of injection of air on 1-butanol was small, but likewise in the same direction. The removal of hydrogen from the catalyst by preinjection of cyclohexene caused no similar effect to that of air.

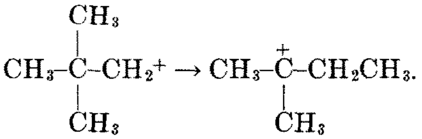
The effect of injection of air could be interpreted by assuming that through the oxidation of the metal new basic sites are being created. Since the formation of ethers from alcohols depends on the coordinative action of both acidic and basic sites, the proper balance of the two sites is essential for the high yields of ether.

DISCUSSION OF RESULTS

The dehydration of alcohols to ethers over Pd–Cab-O-Sil catalyst can best be explained by assuming that intrinsic acidic and basic sites are present on the catalyst and these sites participate coordinatively to form ethers. The formation of dineopentyl ether in 73% yield from neopentyl alcohol gives best support to this mechanism:



A fully developed cation is presumably not formed during the production of the ether, otherwise a primary neopentyl cation would have undergone a facile skeletal isomerization to the more stable *tert*-pentyl cation:



$$CH_3\text{–}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{–}CH_2^+ \rightarrow CH_3\text{–}\overset{+}{\underset{\displaystyle CH_3}{C}}\text{–}CH_2CH_3.$$

The formation of isopentane in the absence of neopentane as a minor product at 160°C and a major product at 190°C, Table 2, is an indication that a direct

TABLE 4

Effect of Injection of Air over Pd–Cab-O-Sil Catalyst on Reaction of 1-Butanol and 2-Propanol at 160°C[a]

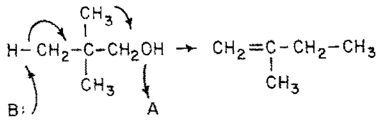
Alcohol	Time elapsed since injection of air (min)[b]	Conversion (%)	Composition of product (mol%)		
			Ether	C_3H_8	C_4H_{10}
1-Butanol	Before	14.2	91.9	2.0	6.1
	20	13.2	96.2	1.5	2.3
	45	13.3	94.7	1.5	3.8
2-Propanol[c]	95	48	79.2	20.8	
	120	50	76.0	24.0	
	180	53	66.0	34.0	
	360	55	52.7	47.3	
2-Propanol	Before	55	52.7	47.3	
	20	27	88.9	11.1	
	40	33	84.5	15.2	
	60	43	83.7	16.3	
	90	47	80.8	19.2	
	120	50	76.0	24.0	
	160	52	69.2	30.8	
	220	54	61.1	38.9	
	340	55	52.7	47.3	

[a] Conditions the same as in Table 1, footnote *a*.

[b] Air injected, 50 ml.

[c] This experiment is a direct continuation of the experiment with 1-butanol.

hydrogenolysis of the hydroxyl groups in primary alcohols does not occur. The formation of isopentane from neopentyl alcohol could best be explained as occurring via dehydration in which both intrinsic acidic and basic sites of the catalyst participate



$$H{-}CH_2{-}C(CH_3)_2{-}CH_2OH \rightarrow CH_2{=}C(CH_3){-}CH_2{-}CH_3$$

This type of participation was reported by one of us to occur in the dehydration of primary alcohols over alumina (*12*).

The formation of isopentane could also be ascribed, although less likely, to the hydrogenolysis of 1,1-dimethylcyclopropane, a product detected in the dehydration of neopentyl alcohol over alumina (*13*) and over reduced nickel oxide (*5*). An independent study of the hydrogenolysis of 1,1-dimethylcyclopropane under experimental conditions specified in Table 2 revealed, however, that the pentanes produced consisted primarily of neopentane, and to a smaller extent of isopentane (*14*). A more direct proof that 1,1-dimethylcyclopropane is not the intermediate in the formation of isopentane was obtained from the reaction of 1-^{13}C labeled neopentyl alcohol. The alcohol was prepared in about 50% yield by the following steps:

$$(CH_3)_3CMgCl + {}^{13}CO_2 \rightarrow$$
$$(CH_3)_3C^{13}CO_2MgCl \xrightarrow[H_2SO_4]{CH_3OH}$$
$$(CH_3)_3C^{13}CO_2CH_3 \xrightarrow{LiAlH_4}$$
$$(CH_3)_3{}^{13}CCH_2OH$$

The nmr analysis showed that the ^{13}C was concentrated predominantly in C-3 position of the isopentane, although there was some enrichment in C-4 position. This indicates that a small amount of 1,1-dimethylcyclopropane could have been formed in the reaction over Pd on Cab-O-Sil. The absence, however, of neopentane in the product excludes such an assertion.

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