INVESTIGATION OF THE HYDROGENATION OF p-CARBOXYBENZALDEHYDE IN THE PRESENCE OF Pd-, Ru-, AND Rh-CATALYSTS

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The catalytic hydrogenation of an aromatic aldehyde may include a series of steps: reduction of the aldehyde group, hydrogenolysis of the C-OH bond of the carbinol formed, hydrogenation of the aromatic ring. From the literature data it follows that the dependence of the direction of the reaction and the ratio of the rates of the individual steps on the nature of the catalyst and the conditions of the process has been investigated for the example of benzaldehyde [1, 2].

In this work we studied the conversion of p-carboxybenzaldehyde under conditions of catalytic hydrogenation. This reaction can also be used as a method of purification of terephthalic acid from p-carboxybenzaldehyde.

EXPERIMENTAL METHOD

p-Carboxybenzaldehyde (purity 99.0%) was synthesized through ω -dichloromethylbenzoyl chloride. The catalysts were prepared by applying the salt (PdCl₂, ruthenium hydroxochloride, or RhCl₃) on activated charcoal or γ -Al₂O₃, followed by reduction with H₂: palladium at 20°, ruthenium at 300°, rhodium at 250°. The experiments were conducted in a thermostatically controlled glass reactor at 50°, atmospheric pressure, and intensive mixing. The temperature was maintained with an accuracy of ±0.05°. For each experiment we took 0.1-1.0 g of the aldehyde, 25 ml of the solvent, and 0.5 g of the catalyst, containing 0.5% Pd or 5% Rh, Ru, applied on activated charcoal or γ -Al₂O₃.



Fig.1. Dependence of the initial rate of hydrogenation of p-carboxybenzaldehyde on the pressure of H_2 . Aldehyde 0.3 g; Pd/C; solvent ethanol.

Fig.2. Kinetic data on the hydrogenation of p-carboxybenzaldehyde in the presence of 0.5% Pd/C (1) or Pd/ γ -Al₂O₃ (1') and benzaldehyde on Pd/C (2) or Pd/ γ -Al₂O₃ (2'). The conditions are given in the caption to Fig.1.

N.D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp.1738-1742, August, 1972. Original article submitted March 26, 1971.

© 1973 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00. TABLE 1. Relative Activity of Catalysis in the Hydrogenolysis of p-Carboxybenzyl Alcohol

Catalyst	Solvent	Activity A* , 10 ³ , moles/min • g	Hydro- genolysis	
			degree, %	time, min
Pd/C	H ₂ O	500	100	8
(0,5%) Rh/C		0,7	68	80
(5%) Ru/C		0,3	28	80
(5%) Pd/C	C_2H_5OH	430	100	12
(0,5%) Rh/C		2,1	100	80
(5%) Ru/C		0,0	0,0	80
(5%) Pd/C	сн₃соон	340	100	10
(0, 5%) Rh/C		0,3	30	80
(5%) Ru/C		0,0	0,0	80
(5%)	1	1	1	

* The activity was estimated according to the initial rate of conversion of the alcohol.

TABLE 2. Influence of Solvent on the Rate of Hydrogenation of p-Carboxybenzaldehyde

Solvent	Rate of ab- sorption of H ₂ , m1/min		ctric Int at
	1 *	2†	Diele consta 25° [5
Benzene Ethanol Dioxane Methanol Ethyl acetate Acetone Acetic acid Water Dimethylformamida	0,0 38,0 0,0 27,5 7,0 15,0 26,0 40,0 3,0	$\begin{array}{c} 0, 0 \\ 15, 0 \\ 0, 0 \\ 14, 0 \\ 2, 5 \\ 1, 5 \\ 13, 0 \\ 20, 0 \\ 0 \end{array}$	2,28 24,30 2,2 32,63 6,02 20,70 6,15 80,0 37,60

*At the moment of absorption of 0.4 mole. †At the moment of absorption of 1.4 moles. During the process of hydrogenation we measured the rate of absorption of H_2 and collected samples of the catalyzate for chromatographic and polarographic [3] determinations of the unreacted p-carboxybenzaldehyde.

DISCUSSION OF RESULTS

Hydrogenation of Pd/C (0.5%). The Pd catalyst proved most active, which agrees with the literature data for other aromatic aldehydes. The initial rate of absorption of H_2 did not depend on the concentration of carboxybenzaldehyde within the range 0.2-0.5 g. Lowering the partial pressure of H_2 (in dilution with Ar) leads to a linear decrease in the initial reaction rate (Fig.1). Thus, the reaction is characterized by zero order with respect to the substrate and first order with respect to H_2 .

During the hydrogenation of the aldehyde, a decrease in the reaction rate is observed as a result of partial poisoning of the catalyst, and not on account of the deviation from zero order. This is evident from the independence of the initial reaction rate from the concentration of p-carboxybenzaldehyde and confirmed by the fact that in the successive hydrogenation of several samples of aldehyde on the same portion of the catalyst, the initial rate also decreases.

It is known that in the hydrogenation of certain aromatic aldehydes and ketones on a Pd-catalyst, the hydrocarbon formed may inhibit the reaction. Actually, an individual experiment established that the introduction of p-toluic acid into the reaction mixture inhibits the process. The cause of the poisoning of the catalyst may also be the formation of condensation products, capable of blocking the active surface of the catalyst, as was observed in the hydrogenation of other aromatic aldehydes on a Pd-catalyst [4].

Polarographic and chromatographic analyses have shown that after the absorption of 1 mole of H_2 , no more than 1% of the initial aldehyde remains in the catalyzate. The reaction does not stop at this stage. The total amount of absorbed H_2 approaches 2 mole/mole of the aldehyde. Consequently, the hydrogenation of p-carboxybenzal-dehyde on this catalyst under mild conditions proceeds strictly successively in two steps: reduction of the aldehyde group to an alcohol group and hydrogenolysis of the alcohol formed.

A comparison of the kinetic curves of the hydrogenation of pcarboxybenzaldehyde and unsubstituted benzaldehyde (Fig. 2) shows that the introduction of a carboxyl group has an appreciable influence

on the process: the reaction rate approximately doubles. The change in the nature of the carrier $(\gamma-Al_2O_3)$ instead of activated charcoal) leads not only to a decrease in the value of the specific surface), but also to an increase in its selectivity. We should note that in the hydrogenation of benzaldehyde on Pd/C, no decrease in the reaction rate at the first step is observed.

Influence of the Nature of the Catalyst. Ru and Rh differ substantially from Pd in activity. The kinetic curves (Fig. 3) show that this difference is maintained for different solvents. The catalysts studied differ especially sharply with respect to the second step of the reaction (hydrogenolysis of the p-carboxybenzyl alcohol formed). From Table 1 it is evident that in the presence of Ru, hydrogenolysis of the C-OH bond occurs very slowly and only in aqueous solution. On a Rh-catalyst, hydrogenolysis proceeds to completion only in ethanol. In this case the amount of absorbed H_2 exceeds 2 moles, i.e., the aromatic ring is also partially hydrogenated.

The results obtained show that the ratio of the rates of the successive reactions of reduction of the aldehyde group and hydrogenolysis of the C-OH bond depends on the nature of the catalyst and the nature



Fig.3. Comparative activity of catalysts in the hydrogenation of pcarboxybenzaldehyde: 1) Pd/C (0.5%); 2) Ru/C (5%); 3) Rh/C (5%). a) Ethanol; b) water; c) acetic acid.

Fig. 4. Kinetic curves of the hydrogenation of p-carboxybenzaldehyde in various solvents (aldehyde 0.3 g; Pd/C): 1) water; 2) ethanol; 3) methanol; 4) acetic acid; 5) buffer solution (1.2 M CH₃COONa + 0.2 M CH₃COOH); 6) acetone; 7) ethyl acetate; 8) dimethylformamide; 9) 80% ethanol with an addition of 0.5 g NaOH.

of the solvent. Evidently these processes occur according to different mechanisms; therefore the selectivity of the process can be varied within broad limits by varying the conditions of the reaction. The use of Pd, the activity of which is two orders of magnitude higher than that of the other catalysts, permits reduction of the aldehyde group to the methyl group. In the presence of Ru, p-carboxybenzyl alcohol can be obtained in a high yield under mild conditions. Comparison with the literature data for benzyl alcohol gives a basis for believing that under rigorous conditions the aromatic ring can also be reduced on this catalyst, with conservation of the hydroxyl group.

Influence of the Nature of the Solvent. Figure 4 and Table 2 present data on the hydrogenation of pcarboxybenzaldehyde in various solvents on Pd/C (0.5%). It was found that the rate of reduction of the aldehyde group decreases in the series: water > ethanol > methanol > acetic acid > acetone > ethyl acetate > dimethylformamide, while in benzene, acid, and dioxane the reaction does not take place. The addition of these solvents to ethanol leads to an appreciable lowering of the rate. In hydrogenation in buffer solution (CH₃COONa - 1.2 M + CH₃COOH - 0.2 M), hydrogenolysis of the alcohol formed practically does not occur (see Fig. 4, curve 5). When the pH is further increased (alcoholic alkali), the total rate of the process is sharply reduced. Evidently a definite role is played the acid -base properties of the medium, as well as the ability of the solvent to be adsorbed on the catalyst. For example, aromatic hydrocarbons may compete with an aromatic aldehyde in adsorption, displacing the latter.

A comparison of the kinetic data with the values of the dielectric constant of the solvents shows the presence of some correlation; in most cases with decreasing dielectric permeability the reaction rate decreases. However, in dimethylformamide the reaction proceeds at a minimum rate, and in acetic acid at a high rate.

It is interesting to note that in the hydrogenolysis of $C_6H_5CH_2OH$ on Pd/C (0.5%), a decrease in the rate was observed in the series: acetic acid > water > methanol > ethyl acetate > hexane [6].

CONCLUSIONS

1. The hydrogenation of p-carboxybenzaldehyde proceeds according to zero order with respect to the substrate and according to first order with respect to H_2 .

2. On Pd-catalysts, hydrogenation is accompanied by subsequent hydrogenolysis of the C-OH bond of the carbinol formed.

3. On a Rh-catalyst hydrogenolysis proceeds extremely slowly, while on a Ru-catalyst p-carboxybenzyl alcohol is selectively formed.

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