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Hydrogenation and Hydrogenolysis. IX.[1] The Hydrogenation of Benzyl Alcohol with Platinum Metal Catalysts

By Shigeo NISHIMURA and Michiko HAMA

Department of Industrial Chemistry, Tokyo University of Agriculture and Technology, Koganei, Tokyo

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The rate of the hydrogenation of benzyl alcohol with a rhodium catalyst decreases markedly in the course of the reaction, accompanied by the formation of an increasing amount of cyclohexanecarboxaldehyde with the conversion of the alcohol. The decrease in the rate is only slight with a platinum catalyst, however, and the formation of the aldehyde is much less than with the rhodium catalyst. It has been shown that cyclohexanecarboxaldehyde is an effective catalyst poison in the hydrogenation of benzyl alcohol, but that cyclohexylcarbinol is not. 1-Cyclohexenylcarbinol, an intermediate of the hydrogenation, isomerizes to cyclohexanecarboxaldehyde during the hydrogenation on rhodium and 7 : 3 rhodium-platinum catalysts to a greater extent than on the platinum catalyst. Cyclohexanecarboxaldehyde is hydrogenated only very slowly, but the rate with the platinum catalyst is about four times greater than that with the rhodium catalyst. These results may account for the different behaviors of the rhodium or 7 : 3 rhodium-platinum catalyst and the platinum catalyst observed in the hydrogenation of benzyl alcohol.

It has been reported in a previous paper that the hydrogenation of benzyl alcohol to cyclohexylcarbinol is not successful with a rhodium-platinum catalyst because of a marked decrease in the rate in the course of the reaction,[2] although benzyl ethers, benzyl acetate and α-substituted benzyl alcohols are easily hydrogenated to give good yields of the corresponding saturated compounds with the same catalyst.[2-4] Such a phenomenon was also observed in the hydrogenation with a supported rhodium catalyst.[5] Benzyl alcohol may be hydrogenated to cyclohexylcarbinol in a good yield, either with an Adams platinum catalyst in alcohols containing a small amount of acetic acid[6,7] or, better, with a ruthenium catalyst in the presence of water.[1] The present study was undertaken to elucidate the cause of the deactivation of rhodium and rhodium-platinum catalysts observed in the hydrogenation of benzyl alcohol.

Experimental

Materials.—Benzyl alcohol of the G. R. grade was used after a fresh and careful distillation under reduced pressure. Cyclohexylcarbinol was prepared by the hydrogenation of benzyl alcohol with ruthenium hydroxide catalyst[8] in the presence of water, a typical run being shown in the following: 43 g. of benzyl alcohol was hydrogenated with the addition of 10 ml. of water at 90°C under 80—100 kg./cm^2 of hydrogen pressure, using 0.1 g. of the catalyst. The hydrogen uptake was complete in 3.5 hr. The distillation of the product after extraction with ether gave 37 g. of cyclohexylcarbinol, b. p. 91.5°C/22—23 mmHg (81% yield). Cyclohexanecarboxaldehyde was prepared by the oxidation of cyclohexylcarbinol with chromium trioxide in acetic acid and purified via the sodium hydrogen sulfite adduct.[9] 1-Cyclohexenylcarbinol was prepared by the reduction of methyl 1-cyclohexenecarboxylate[10] with lithium aluminum hydride.[11] The purity of the compounds prepared was well confirmed by means of gas chromatography.

Catalysts.—The oxide catalysts of platinum and 7 : 3 rhodium-platinum were prepared by the Adams method.[12,13] The rhodium hydroxide catalyst was prepared by adding a slight excess of a lithium hydroxide solution to a hot aqueous solution of rhodium chloride, followed by a thorough washing with hot, distilled water.

Hydrogenation. — All the hydrogenations were carried out at 25°C under the atmospheric pressure of hydrogen, using isopropyl alcohol as the solvent. Benzyl alcohol (0.5 g.) and additives were added, together with the solvent, after the metal oxide had been reduced to the metal with hydrogen in the solvent containing a small amount of acetic acid (0.02 ml.), the total amount of the solvent used being 10 ml. Rhodium

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[1] Part VIII: Y. Takagi, T. Naito and S. Nishimura, This Bulletin, **37**, 585 (1964).
[2] S. Nishimura, ibid., **34**, 32 (1961).
[3] S. Nishimura, ibid., **33**, 566 (1960).
[4] S. Nishimura and H. Taguchi, ibid., **36**, 318 (1963).
[5] J. H. Stocker, *J. Org. Chem.*, **27**, 2288 (1962).
[6] S. Nishimura, This Bulletin, **32**, 1155 (1959).
[7] Y. Ichinohe and H. Itō, ibid., **37**, 887 (1964).
[8] Y. Takagi, T. Naito and S. Nishimura, ibid., **38**, 2119 (1965).
[9] N. Zelinsky and J. Gutt, *Ber.*, **40**, 3050 (1907).
[10] W. J. Bailey and R. A. Baylouny, *J. Am. Chem. Soc.*, **81**, 2126 (1959).
[11] B. Lythgoe, S. Trippett and J. C. Watkins, *J. Chem. Soc.*, **1956**, 4060.
[12] R. Adams, V. Voorhees and R. L. Shriner, "Organic Syntheses," Coll. Vol. I, 2nd Ed., 463 (1941).
[13] S. Nishimura, This Bulletin, **34**, 1544 (1961).

hydroxide was reduced to metal in isopropyl alcohol without the addition of acetic acid, since the presence of the acid greatly retarded the reduction of the hydroxide and since the hydrogenation of benzyl alcohol with this catalyst occurred without the addition of acetic acid.[14] Hydrogenation products were analyzed directly by gas chromatography using a column containing PEG-6000.

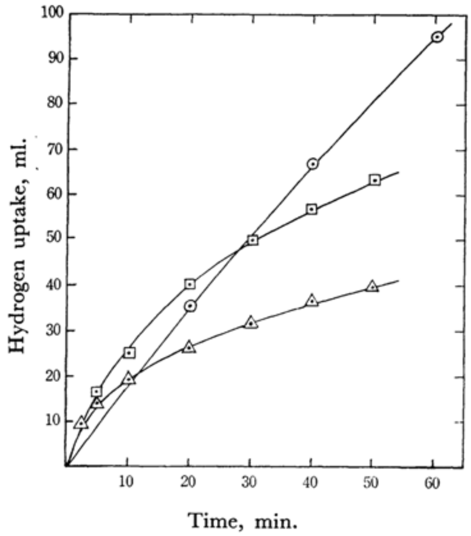

Fig. 1. Hydrogenation of benzyl alcohol.
- ⊡ Hydrogen uptake with rhodium catalyst
- ◬ Hydrogen uptake with 7: 3 rhodium-platinum catalyst
- ⊙ Hydrogen uptake with platinum catalyst

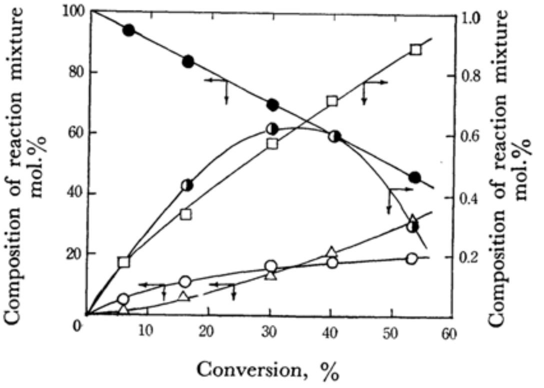

Fig. 2. Products of the hydrogenation of benzyl alcohol with rhodium catalyst.
- □ Cyclohexanecarboxaldehyde
- ○ Cyclohexylcarbinol
- ◑ 1-Cyclohexenylcarbinol
- △ Toluene
- ● Benzyl alcohol

Results and Discussion

The hydrogen uptake in the hydrogenation of benzyl alcohol with rhodium, 7 : 3 rhodium-platinum and platinum catalysts is shown in Fig. 1. It may be seen that the rate of the hydrogenation decreases markedly in the course of a reaction with the rhodium and 7 : 3 rhodium-platinum catalysts. The decrease in the rate is only slight with the platinum catalyst, however. Figures 2 and 3 show the changes in the amounts of the products formed in the course of the hydrogenation with the rhodium catalyst and with the platinum catalyst respectively. The most pronounced difference in the products seems to be that, with the rhodium catalyst, the formation of cyclohexanecarboxaldehyde is much greater than with the platinum catalyst and that it increases with conversion, whereas with the platinum catalyst the aldehyde is formed in an amount only 0.1% of the reaction mixture, even at the maximum, and then decreases gradually after about a 40% conversion. 1-Cyclohexenylcarbinol was also detected in the course of the rhodium-catalyzed hydrogenation, but it decreased rapidly after about 40% conversion.

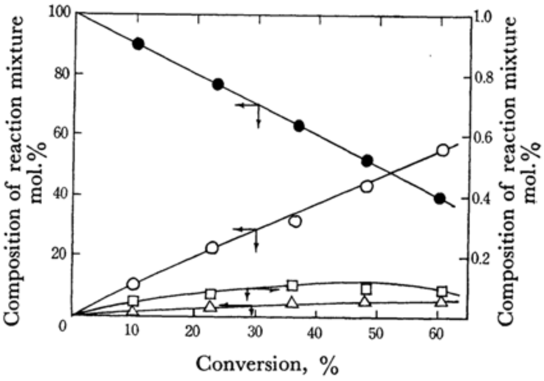

Fig. 3. Products of the hydrogenation of benzyl alcohol with platinum catalyst.
- □ Cyclohexanecarboxaldehyde
- ○ Cyclohexylcarbinol
- △ Toluene
- ● Benzyl alcohol

Since it may be supposed from the above results that the cyclohexanecarboxaldehyde formed during the hydrogenation may be a catalyst poison, the effect of the addition of the aldehyde was then studied and compared with the effect of added cyclohexylcarbinol (Fig. 4). It may be seen that the hydrogenation of benzyl alcohol is markedly inhibited by the addition of cyclohexanecarboxaldehyde, while the addition of cyclohexylcarbinol has little effect on the rate of the hydrogenation. The effect of the addition of 1-cyclohexenylcarbinol

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[14] The rhodium hydroxide catalyst used in this study probably contains a much smaller amount of alkaline substances than the oxide catalysts of the Adams type (cf. Ref. 8).

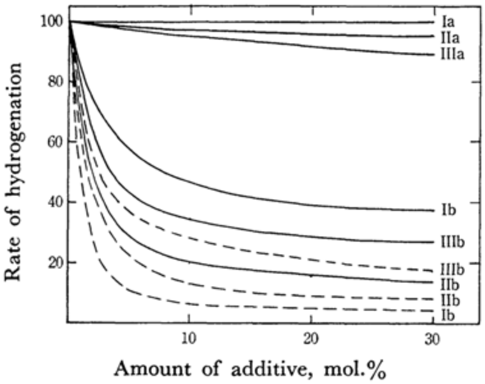

Fig. 4. The effects of added cyclohexylcarbinol and of cyclohexanecarboxaldehyde in the hydrogenation of benzyl alcohol.
I: Rhodium II: 7:3 Rhodium-platinum
III: Platinum a: Cyclohexylcarbinol
b: Cyclohexanecarboxaldehyde
——: Added in mixture with benzyl alcohol
- - -: Added before the addition of benzyl alcohol

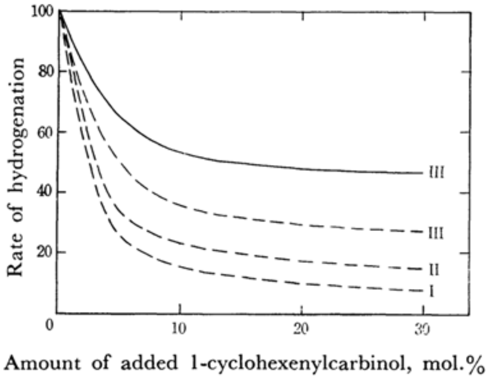

Fig. 5. The effect of the addition of 1-cyclohexenylcarbinol on the rate of the hydrogenation of benzyl alcohol.
I: Rhodium II: 7:3 Rhodium-platinum
III: Platinum
——: Added in mixture with benzyl alcohol
- - -: Added before the addition of benzyl alcohol

was also studied (Fig. 5), since the unsaturated alcohol is produced as an intermediate of the hydrogenation and is probably the precursor of the aldehyde formed in the hydrogenation.

It may be seen from Fig. 5 that the addition of 1-cyclohexenylcarbinol also inhibits the hydrogenation, although to a somewhat lesser extent than in the case of cyclohexanecarboxaldehyde. It may also be seen that the decrease in the rate is more pronounced in the hydrogenation with the rhodium catalyst than with the platinum catalyst. It should be noted that the hydrogenation is more retarded when the compounds are added before the addition of benzyl alcohol than when they are previously admixed with benzyl alcohol, as is shown in Figs. 4 and 5. Table I shows the products of the hydrogenation of 1-cyclohexenylcarbinol with rhodium, 7 : 3 rhodium-platinum and platinum catalysts. The hydrogenations with rhodium and and 7 : 3 rhodium-platinum catalysts are accompanied by the formation of cyclohexanecarboxaldehyde (about 18%). Such an isomerization occurs to a much lesser extent with the platinum catalyst (about 5%).(15) Thus, the action of cyclohexenylcarbinol as a catalyst poison probably results from the formation of the aldehyde by isomerization during the hydrogenation. The hydrogenation of the aldehyde was found to occur only very slowly, especially with the rhodium catalyst (hydrogen uptake: 3 ml./hr., 50 mg. catalyst). With the platinum catalyst the aldehyde is hydrogenated at a rate about four times greater than with the rhodium catalyst.

TABLE I. PRODUCTS OF THE HYDROGENATION OF 1-CYCLOHEXENYLCARBINOL

Catalyst	Product, %		
	Cyclohexylcarbinol	Cyclohexanecarboxaldehyde	Hydrocarbons
Platinum[a]	94.8	5.2	Trace
7:3 Rhodium-Platinum	75.0	18.1	6.9
Rhodium	75.9	17.8	6.3

a) Products obtained in 84% hydrogenation.

From the results described above, it is very probable that the deactivation observed in the hydrogenation of benzyl alcohol with rhodium and rhodium-platinum catalysts is caused by the cyclohexanecarboxaldehyde formed by the isomerization of 1-cyclohexenylcarbinol, which is expected to be produced in a considerable amount as an intermediate of the hydrogenation, although the amount of it detected in the course of the hydrogenation was rather small.(16) The hydrogenation with the platinum catalyst is only slightly poisoned, because the isomerization of 1-cyclohexenylcarbinol occurs to a much lesser extent and the aldehyde formed by the isomerization is hydrogenated much faster than with the rhodium catalyst. It is known that ruthenium catalysts hydrogenate aliphatic aldehydes to alcohols with ease;(17,18)

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15) The hydrogenation with the palladium hydroxide catalyst was accompanied by an extensive hydrogenolysis, affording 74% of methylcyclohexane along with 20.5% of cyclohexylcarbinol, 1.6% of cyclohexanecarboxaldehyde, and other products.

16) Cf. S. Siegel, G. V. Smith, B. Dmuchovsky, D. Dubbell and W. Halpern, *J. Am. Chem. Soc.*, **84**, 3136 (1962).

17) G. Gilman and G. Cohn, "Advances in Catalysis," Vol. IX, Academic Press, New York (1957), p. 733.

18) Y. Takagi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **57**, 105 (1963).

this may account for the rapid hydrogenation of benzyl alcohol with these catalysts. The formation of cyclohexanecarboxaldehyde is not possible, at least in the absence of water, in the hydrogenation of benzyl ethers and esters, which are both hydrogenated easily with rhodium and rhodium-platinum catalysts. α-Substituted benzyl alcohols, which are also hydrogenated rapidly with rhodium and rhodium-platinum catalysts,[2-5] may give saturated ketones in the course of the hydrogenation, but it is probable that the adsorption of ketones on catalyst metals will not be so strong as that of aldehydes[19] and that the hydrogenation of ketones may occur more rapidly than in the case of aldehydes.[2,20]

It is an interesting fact that the ratio of the toluene to the cyclohexylcarbinol formed in the hydrogenation of benzyl alcohol increases with conversion with the rhodium catalyst, while it is nearly unchanged during the hydrogenation with the platinum catalyst (see Figs. 2 and 3). This suggests that the hydrogenation of the benzene nucleus is more inhibited by the presence of cyclohexanecarboxaldehyde than is the hydrogenolysis of the hydroxyl group. This is further supported by the observation that the hydrogenolysis of benzyl alcohol with a palladium catalyst is not inhibited at all by the addition of the aldehyde.

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[19] The hydrogenation of benzyl alcohol with the rhodium catalyst was not retarded at all, even by the addition of 30 mole% of acetone (unpublished).

[20] E. Beitner, E. Roginsky and P. N. Rylander, *J. Org. Chem.*, **24**, 1955 (1959).