Hydrogenation and Hydrogenolysis. III⁽¹⁾. *Rhodium-Platinum Oxide as a Catalyst for the Hydrogenation of the Aromatic Nucleus*

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(Received March 10, 1960)

It has been shown in these two decades that rhodium is useful as a catalyst for the hydrogenation of various organic compounds[2], and recently that it is specially effective for the hydrogenation of the aromatic nucleus[3-5]. However, most of the works on rhodium catalysts are concerned with the use of colloidal or supported rhodium, and none with the use of rhodium oxide of Adams' type. It seem that this is because of the difficulty of reducing rhodium oxide to the metal form under mild conditions[6].

The present author prepared a useful catalyst consisting of rhodium oxide and platinum oxide in a ratio of 3 : 1 by the weights of the metals, by fusion of the mixture of rhodium chloride and chloroplatinic acid or ammonium chloroplatinate with sodium nitrate exactly in the same way as in the preparation of Adams platinum oxide[7]. This rhodium-platinum oxide[8] can be reduced with hydrogen to rhodium-platinum

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[1] Part II of this series: S. Nishimura, This Bulletin, 32, 1155 (1959).

[2] For earlier literatures, see Refs. 3 and 5.

[3] L. D. Freedman, G. O. Doak and E. L. Petit, *J. Am. Chem. Soc.*, 77, 4262 (1955).

[4] H. A. Smith and R. G. Thompson, "Advances in Catalysis", Vol. 9, Academic Press Inc., New York (1957), p. 727.

[5] G. Gilman and G. Cohn, ibid., p. 733.

[6] Cf. Ref. 4, p. 732. This difficulty was also confirmed by the present author.

[7] R. Adams, V. Voorhees and R. L. Shriner, "Organic Syntheses", Col. Vol. 1, 2nd Ed., John Wiley & Sons, Inc., New York (1941), p. 463.

[8] The mixed oxide thus prepared is not identical with the mere mixture of rhodium oxide and platinum oxide, the former being reduced with hydrogen much more rapidly and uniformly than the latter.

black in neutral ethanolic or acetic acid suspension at the ordinary temperature and pressure. The reduction begins in about twenty minutes and completes in about forty minutes in acetic acid at 25°C. The rhodium-platinum black thus prepared is an excellent catalyst in the hydrogenation of various aromatic compounds in acetic acid under ordinary conditions as shown in Table I. With this catalyst, methylphenylcarbinol, benzhydrol, phenol, anisole and cinnamyl alcohol are reduced rapidly and quantitatively to the corresponding saturated compounds with far less portions of hydrogenolysis than with Adams platinum oxide as indicated by the moles of hydrogen absorbed. The catalyst is four and six times as active as Adams platinum oxide in the hydrogenation of benzene and ethyl benzoate, respectively, where the hydrogen uptake is equally 3 mol. with both catalysts. Thus the results show that the rhodium-platinum catalyst retains to a large extent the nature of pure rhodium catalysts and is substantially superior to Adams platinum oxide both in activity and in selectivity in the hydrogenation of the aromatic nucleus. Details will follow.

TABLE I. HYDROGENATION OF AROMATIC COMPOUNDS WITH RHODIUM-PLATINUM OXIDE AND PLATINUM OXIDE AS CATALYSTS AT THE ORDINARY TEMPERATURE AND PRESSURE[a]

Compound	Amount, g.	Catalyst, g.	Hydrogen uptake, mol./mol.	Time for complete hydrogenation, min.
Methylphenylcarbinol	0.611	Rh-Pt, 0.05	3.04	36
〃	〃	Pt, 0.20	3.87	80
Benzhydrol	0.553	Rh-Pt, 0.05	6.03	105
〃	〃	Pt, 0.20	6.73	120
Phenol	0.471	Rh-Pt, 0.05	3.04	14
〃	〃	Pt, 〃	3.35	40
Anisole[b]	0.541	Rh-Pt, 〃	3.04	18
〃	〃	Pt, 〃	3.45	85
Cinnamyl alcohol[c]	1.342	Rh-Pt, 〃	1.04	11
〃	〃	Pt, 〃	1.31	26
Benzene[d]	0.781	Rh-Pt, 〃	2.99	20
〃	〃	Pt, 〃	2.99	80
Ethyl benzoate	0.751	Rh-Pt, 〃	3.02	21
〃	〃	Pt, 〃	3.00	120

a) 20 cc. of glacial acetic acid was used as solvent.

b) Smith and Thompson (Ref. 4) reported that anisole absorbed 3.06 mol. of hydrogen with 5% rhodium on alumina and 3.40 mol. with Adams platinum oxide in acetic acid at 30°C under initial hydrogen pressures of 40–60 p. s. i.

c) Reduction to 3-phenyl-1-propanol and propylbenzene.

d) Gilman and Cohn (Ref. 5) reported that 5 ml. of benzene was hydrogenated four times as rapidly with 1 g. of 5% rhodium on alumina as with 1 g. of 5% platinum on alumina in acetic acid under ordinary conditions.

The author wishes to express his hearty thanks to Professor Y. Urushibara for his continued encouragement.

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