Hydrogenation and Hydrogenolysis. V[1]. *Rhodium-Platinum Oxide as a Catalyst for the Hydrogenation of Organic Compounds*[2]

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In previous papers[1,2], it was reported that rhodium-platinum oxide, prepared by fusion of the mixture of rhodium chloride and chloroplatinic acid or ammonium chloroplatinate in a ratio of 3 : 1 by the weights of the metals with sodium nitrate exactly in the same way as in the preparation of Adams platinum oxide, can be reduced with hydrogen to the metal form under ordinary conditions and also that the resulting rhodium-platinum black is an excellent catalyst retaining the nature of pure rhodium catalysts and is substantially superior to Adams platinum oxide both in activity and in selectivity in the hydrogenation of various aromatic compounds. The present paper describes the use of the rhodium-platinum oxide as a catalyst and also the comparisons with platinum oxide and with palladous oxide in the hydrogenation of various organic compounds under ordinary conditions.

Experimental

Materials. — The oxide catalysts were prepared according to the procedures described in the preceding paper[1]. Glacial acetic acid of Wakō Pure Chemical Industries G. R. grade was used without further purification. Commercial 95% ethanol was used after distillation. All the substrates were carefully purified before use by recrystallization or by distillation.

Hydrogenation.—Hydrogenation was carried out under atmospheric pressure and at room temperature (24~26°C). After the oxide was reduced to metal, the substance was added with a small amount of solvent, and the mixture was shaken with hydrogen at about 350~400 oscillations per minute.

Results and Discussion

Catalytic Reduction, where the C-O Linkage is Liable to Hydrogenolysis. — As already reported in previous papers[1,2], the compounds, which have C-O linkages susceptible to hydrogenolysis, are less hydrogenolyzed and much more rapidly hydrogenated in acetic acid with rhodium-platinum oxide than with platinum oxide[3]. Further results are shown in Tables I and II, and also the hydrogenation of acetophenone in Table III and furfuryl alcohol in Table IV. If less hydrogenolysis is desired, it is preferable to use ethanol with a small amount of acetic acid as the solvent, as shown in the hydrogenation of benzyl methyl ether[4]. Benzyl acetate is almost completely hydrogenolyzed even under these conditions. The addition of a slight amount of hydrochloric acid increases the hydrogenolysis as shown in the hydrogenation of hydroquinone with platinum oxide[5].

Aliphatic and alicyclic ketones are also less hydrogenolyzed and much more rapidly hydrogenated with rhodium-platinum oxide than with platinum oxide in acetic acid (Table II).

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[1] Part IV of this series: S. Nishimura, T. Onoda and A. Nakamura, This Bulletin, 33, 1356 (1960).

[2] Cf. Part III of this series: S. Nishimura, ibid., 33, 566 (1960).

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

[4] Cf. S. Nishimura, This Bulletin, 32, 1155 (1959).

[5] For the effect of the solvent on the hydrogenation and hydrogenolysis, see, for instance, Ref. 1.

TABLE I. CATALYTIC REDUCTION OF AROMATIC COMPOUNDS WHERE THE C–O LINKAGE IS LIABLE TO HYDROGENOLYSIS

Compound, g.	Solvent, ml.	Catalyst, g.	Hydrogen uptake mol./mol.	Time for hydrogenation min.
Benzyl methyl ether, 0.611	EtOH, 20	Rh-Pt oxide, 0.10	S.*	
〃	〃	Pt oxide, 0.20	S.*	
〃	EtOH, 20+ AcOH, 0.02	Rh-Pt oxide, 0.10	3.13	120
〃	〃	Pt oxide, 0.20	3.13	240
〃	AcOH, 20	Rh-Pt oxide, 0.05	3.48	80
〃	〃	Pt oxide, 0.05	3.89	130
Benzyl alcohol, 0.541	〃	Rh-Pt oxide, 0.05	I.**	
〃	〃	Pt oxide, 0.05	3.95	120
Benzyl acetate, 0.751	〃	Rh-Pt oxide, 0.05	3.94	14
〃	〃	Pt oxide, 0.05	3.99	60
Hydroquinone, 1.101	AcOH, 30	Rh-Pt oxide, 0.05	3.25	40
〃	〃	Pt oxide, 0.05	4.01	110
〃	AcOH, 30+ 3 N HCl, 0.1	〃	4.59	120
Methyl salicylate, 0.761	AcOH, 20	Rh-Pt oxide, 0.10	3.13	65
〃	〃	Pt oxide, 0.10	3.26	200
α-Naphthol, 0.721	〃	Rh-Pt oxide, 0.10	5.17	270
〃	〃	Pt oxide, 0.10	5.16	300
β-Naphthol, 0.721	〃	Rh-Pt oxide, 0.10	5.21	85
〃	〃	Pt oxide, 0.10	5.37	275

* Slow reduction.

** Incomplete reduction because of the decreasing rate.

TABLE II. CATALYTIC REDUCTION OF ALIPHATIC AND ALICYCLIC KETONES

Compound, g.	Solvent, ml.	Catalyst, g.	Hydrogen uptake mol./mol.	Time for hydrogenation min.
Diethyl ketone, 0.861	AcOH, 20	Rh-Pt oxide, 0.05	1.01	140
〃	〃	Pt oxide, 〃	1.01	150
Cyclohexanone, 0.981	〃	Rh-Pt oxide, 〃	1.03	7
〃	EtOH, 20	Pt oxide, 〃	1.00	80
〃	AcOH, 20	〃 〃	1.27	30
〃	AcOH, 20+ 3 N HCl, 0.1	〃 〃	1.31	24
Cyclopentanone, 0.841	AcOH, 20	Rh-Pt oxide, 〃	1.08	40
〃	〃	Pt oxide, 〃	1.56	200
Ethyl acetoacetate, 1.302	〃	Rh-Pt oxide, 〃	1.11	15
〃	〃	Pt oxide, 〃	1.56	300

In neutral ethanolic solution these ketones are hydrogenated quantitatively with platinum oxide to the corresponding alcohols with the absorption of just one mole of hydrogen, and the addition of hydrochloric acid increases hydrogenolysis, though only to a small extent, as shown in the hydrogenation of cyclohexanone. As is well known, palladous oxide is practically ineffective for the hydrogenation of these ketones. Details of the hydrogenation and hydrogenolysis of aliphatic and alicyclic ketones will be published later.

Catalytic Reduction of Acetophenone (Table III).—Acetophenone is reduced with rhodium-platinum oxide to cyclohexylmethylcarbinol quantitatively in ethanol and almost quantitatively in acetic acid. The hydrogenation is especially rapid in the latter solvent accompanied only by a slight hydrogenolysis (6%). With platinum oxide, in ethanol as the solvent, one mole of hydrogen is absorbed rather rapidly and further reduction occurs only very slowly, and in acetic acid as the solvent, as much as 84% is hydrogenolyzed to give ethylcyclohexane as indicated by the hydrogen uptake. Both platinum oxide and palladous oxide show the greatest activity for the reduction to ethylbenzene in the presence of acetic acid with

TABLE III. CATALYTIC REDUCTION OF ACETOPHENONE

Acetophenone g.	Solvent, ml.	Catalyst, g.	Hydrogen uptake mol./mol.	Time for hydrogenation min.
0.601	EtOH, 20	Rh-Pt oxide, 0.05	3.98	8/1 mol. 130/4 mol.
〃	〃	Pt oxide, 〃	S. after 1 mol.	25/1 mol.
〃	AcOH, 20	Rh-Pt oxide, 〃	4.06	24
〃	〃	Pt oxide, 〃	4.84	110
〃	AcOH, 20+ 3 N HCl, 0.1	Rh-Pt oxide, 〃	S.	
〃	〃	Pt oxide, 〃	5.03	16/2 mol. 120/5 mol.
1.201	EtOH, 20	Pd oxide, 〃	1.98	20/1 mol. 200/2 mol.
〃	AcOH, 20	〃 〃	1.98	15/1 mol. 60/2 mol.
〃	AcOH, 20+ 3 N HCl, 0.1	〃 〃	1.99	14/1 mol. 30/2 mol.

Reduction on a preparative scale

Acetophenone g.	Solvent ml.	Catalyst, g.	Reactivation with air	Hydrogen uptake mol./mol.	Time hr.	Time min.	Product
12.01	AcOH, 50	Rh-Pt oxide, 0.2	twice	4.06	3	30	Cyclohexylmethylcarbinol, 80%. B.p. 91°C/22 mmHg; n_D^{19} 1.4652

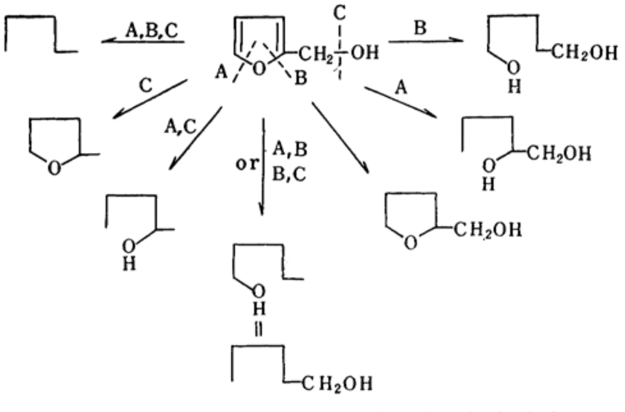

Fig. 1. Catalytic reduction of furfuryl alcohol.

added hydrochloric acid, while the reduction proceeds only very slowly with rhodium-platinum oxide in the same medium. As is well known, palladium is a catalyst preferred for the selective reduction of the side chain because of its low activity for the hydrogenation of the benzene nucleus. Like platinum and palladium catalysts, deactivated rhodium-platinum is also reactivated by shaking with air, and this process is very effective in the hydrogenation of a larger amount of a substrate.

Catalytic Reduction of Furfuryl Alcohol (Table IV).—The complete hydrogenation of furfuryl alcohol under mild conditions is generally expected to give the seven compounds as the result of various competitive reactions between the hydrogenation of the double bonds and the hydrogenolysis of the three C–O linkages indicated by A, B and C, as illustrated in Fig. 1. The kinds and amounts of the products largely depend on the nature of the catalyst and the solvent used. Both rhodium-platinum oxide and palladous oxide give tetrahydrofurfuryl alcohol quantitatively in acetic acid as well as in ethanol with the absorption of two moles of hydrogen. The reduction proceeds most rapidly with rhodium-platinum oxide in acetic acid. With platinum oxide the reduction could not be completed in ethanol because of the decreasing rate of the hydrogenation. But in acetic acid the reduction proceeds smoothly to completion

Table IV. Catalytic reduction of furfuryl alcohol

Furfuryl alcohol g.	Solvent, ml.	Catalyst, g.	Hydrogen uptake mol./mol.	Time for hydrogenation min.
0.981	EtOH, 20	Rh-Pt oxide, 0.05	1.96	42
〃	〃	Pt oxide, 〃	I.	
〃	〃	Pd oxide, 〃	1.95	105
〃	AcCH, 20	Rh-Pt oxide, 〃	1.97	28
〃	〃	Pt oxide, 〃	2.86	115
〃	〃	Pd oxide, 〃	1.96	45
〃	EtOH, 20+ 3 N HCl, 0.1	Pt oxide, 〃	3.11	120
〃	AcOH, 20+ 3 N HCl, 0.1	〃 〃	3.38	85
〃	〃	Pd oxide, 〃	S. after 2.03 mol.	35/2 mol.

Table V. Products of catalytic reduction of furfuryl alcohol with platinum oxide in ethanol (or tetrahydrofurfuryl alcohol) with hydrochloric acid

Product	Yield, %	B. p., °C	n_D^{20}
Pentane*	0.8	35	
2-Methyltetrahydrofuran*	14.8	75～84	1.4031
2-Pentanol	5.5	120～123	1.4047
1-Pentanol	11.6	137～139	1.4096
Tetrahydrofurfuryl alcohol	20.6	173～177	1.4505
1,2-Pentanediol	13.3	110～113/21 mmHg	1.4402
1,5-Pentanediol	3.3	138～142/21 mmHg	1.4499

* These compounds were isolated with the use of tetrahydrofurfuryl alcohol as the solvent.

with an extensive hydrogenolysis as indicated by the absorption of 2.86 mol. of hydrogen[6]. On the other hand, in the presence of hydrochloric acid and ethanol (or tetrahydrofurfuryl alcohol), all the seven compounds were obtained with absorption of 3.11 mol. of hydrogen as shown in Table V[7]. The portion of hydrogenolysis increases further in the presence of acetic acid and hydrochloric acid. With palladous oxide, even in the presence of hydrochloric acid, no hydrogenolysis occurs before the saturation of the double bonds.

Catalytic Reductions of Other Aromatic and Heterocyclic Compounds (Table VI).—Rhodium-platinum oxide is as effective for the hydrogenation of pyridine and quinoline as for aromatic compounds, and substantially more active than platinum oxide also in these hydrogenations. The rhodium-platinum catalyst is also the most active of the three oxides in the hydrogenation of the double bond of the side chain as shown in the hydrogenation of ethyl cinnamate (Table VI) and cinnamyl alcohol (Ref. 1). Palladous oxide is more active in these hydrogenations than platinum oxide.

Catalytic Reduction of Nitrobenzene (Table VII).—Rhodium-platinum oxide is also the most active catalyst in the hydrogenation of nitrobenzene to aniline. Contrary to platinum oxide and palladous oxide, rhodium-platinum oxide is more active in acetic acid than in ethanol. The subsequent hydrogenation of the benzene nucleus proceeds rather slowly both with rhodium-platinum oxide and with platinum oxide in acetic acid. Palladous oxide is almost entirely ineffective for the hydrogenation.

The present results with those reported previously show that the rhodium-platinum (3 : 1) oxide is a substantially more active catalyst than platinum oxide and palladous oxide in the hydrogenation of various organic compounds under ordinary conditions[8], and especially effective where it is desired to avoid hydrogenolysis. Decrease of the platinum in the rhodium-platinum oxide depresses the hydrogenolysis further, but only to a small extent. On

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6) H. A. Smith and J. F. Fuzek, *J. Am. Chem. Soc.*, **71**, 415 (1949), report that 1,2-pentanediol was obtained almost quantitatively under similar conditions.

7) W. E. Kaufmann and R. Adams, *J. Am. Chem. Soc.*, **45**, 3029 (1923), reported that 1-pentanol, 1,2- and 1,5-pentanediols and tetrahydrofurfuryl alcohol were obtained with platinum oxide in the presence of ethanol and a small amount of ferrous chloride with the absorption of 2.5 mol. of hydrogen. Their results show that only the C-O linkages A and B were hydrogenolyzed under these conditions.

8) The metal content of rhodium-platinum (3 : 1) oxide is only 65% of its weight. The value is considerably smaller than those of platinum oxide (80%) and palladous oxide (87%). Therefore, the activity of the rhodium-platinum oxide is much greater when compared in a unit weight of the metal.

TABLE VI. CATALYTIC REDUCTIONS OF OTHER AROMATIC AND HETEROCYCLIC COMPOUNDS

Compound, g.	Solvent, ml.	Catalyst, g.	Hydrogen uptake mol./mol.	Time for hydrogenation min.
Toluene, 0.921	AcOH, 20	Rh-Pt oxide, 0.05	3.02	28
〃	〃	Pt oxide, 〃	3.01	110
Biphenyl, 0.771	〃	Rh-Pt oxide, 〃	5.99	180
〃	〃	Pt oxide, 〃	6.01	440
Ethyl cinnamate, 1.762	〃	Rh-Pt oxide, 〃	4.06	6/1 mol. 65/4 mol.
〃	〃	Pt oxide, 〃	4.01	30/1 mol. 250/4 mol.
〃	〃	Pd oxide, 〃	1.02	10/1 mol.
Pyridine, 0.791	〃	Rh-Pt oxide, 〃	3.01	28
〃	〃	Pt oxide, 〃	3.01	170
Quinoline, 0.646	〃	Rh-Pt oxide, 〃	5.02	80
〃	〃	Pt oxide, 〃	4.98	200

Reduction on a preparative scale

Toluene g.	Solvent ml.	Catalyst, g.	Reactivation with air	Hydrogen uptake mol./mol.	Time		Product
					hr.	min.	
9.21	AcOH, 50	Rh-Pt oxide, 0.2	once	2.99	1	50	Methylcyclohexane, 79%. B. p. 100~101°C

TABLE VII. CATALYTIC REDUCTION OF NITROBENZENE

Nitrobenzene g.	Solvent, ml.	Catalyst, g.	Hydrogen uptake mol./mol.	Time for hydrogenation min.
1.231	EtOH, 20	Rh-Pt oxide, 0.05	S. after 3 mol.	10/3 mol.
〃	〃	Pt oxide, 〃	〃	14/3 mol.
〃	〃	Pd oxide, 〃	3.00	24
〃	AcOH, 20	Rh-Pt oxide, 〃	6.00	6/3 mol. 190/6 mol.
〃	〃	Pt oxide, 〃	5.97	20/3 mol. 230/6 mol.
〃	〃	Pd oxide, 〃	3.00	40

the other hand, the decrease of platinum causes the following disadvantages: (a) It takes a longer time for the reduction of the oxide to the metal. (b) The recovery of the catalyst becomes more difficult, because the residue insoluble in aqua regia increases with the decrease of the platinum[9]. For the reasons mentioned above, the present author chooses the proportion 3:1 of the two metals in the rhodium-platinum oxide as satisfactory for most hydrogenations and convenient for practical use. The fact that the rhodium-platinum oxide is not identical with a mere mixture of rhodium oxide and platinum oxide, the former being reduced with hydrogen much more rapidly and uniformly than the latter, was further confirmed by an X-ray diffraction of these oxides. The peak of rhodium oxide at $2\theta=28°$ (Cu-K_α radiation) disappers completely and most of other peaks of the oxide are greatly deformed in the pattern of rhodium-platinum (3:1) oxide, while the peak of rhodium oxide at 28° and the peak of platinum oxide at 33.3° are clearly detected in the pattern of a mechanical mixture of rhodium oxide and platinum oxide in a ratio of 3:1 by the weights of the metals.

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9) This insoluble residue can be dissolved, e. g., by heating with hydrobromic acid and bromine at 100°C in a sealed tube (" Gmelins Handbuch der Anorganischen Chemie", Vol. 64, Verlag Chemie, G. m. b. H., Berlin (1938), p. 43.).