SHORT COMMUNICATION

High Pressure Hydrogenation with Rhodium-Platinum Oxide

By Shigeo NISHIMURA and Hisaaki TAGUCHI

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In previous papers[1], it was shown that the rhodium-platinum oxide of Adams' type is an excellent catalyst in activity and in selectivity in the hydrogenation of various organic compounds at ordinary temperature and pressure. The effects of platinum in the rhodium-platinum oxide were also reported[2].

Subsequently the use of the rhodium-platinum oxide under high pressure of hydrogen has been found extremely effective in many hydrogenations. Under the pressures of 70 to 100 kg./cm^2, most hydrogenations proceed rapidly at room temperature with (7 : 3) rhodium-platinum oxide (see Table I). Usually in acetic acid rapid absorptions of hydrogen begin with the reduction of the oxide almost instantly at 50°C and in 10 to 30 min. at room temperature at the pressure of 100 kg./cm^2. The rate in hydrogenation of benzene increased greatly with the increase of hydrogen pressure in the range of 75 to 132 kg./cm^2. The activity of (7 : 3) rhodium-platinum oxide under high pressures is not only much greater, but also more stable than that of platinum oxide[3]. Accordingly, with rhodium-platinum oxide only a small amount of the catalyst is required for rapid and complete hydrogenation of most unsaturated organic compounds. With

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[1] S. Nishimura, This Bulletin, 33, 566 (1960); 34, 32 (1961).

[2] S. Nishimura, ibid., 34, 1544 (1961).

[3] High pressure hydrogenations with platinum oxide were reported to be effective [R. H. Baker and R. D. Schuetz, *J. Am. Chem. Soc.*, 69, 1250 (1947)]. But in most cases, for the completion of hydrogenations within a short time, fairly a good amount of the catalyst must be used because of the decrease of the activity during hydrogenation.

TABLE I. HIGH PRESSURE HYDROGENATION WITH (7 : 3) RHODIUM-PLATINUM OXIDE[a]

Compound	Amount g.	Catalyst g.	Temp. °C	H_2 press. kg./cm^2	Time min.	Product (Yield, %)
Benzene	7.81	0.05*	24	75∼49	11	Cyclohexane (Not isolated)
Benzene	7.81	0.05*	24	99∼70	8	Cyclohexane (Not isolated)
Benzene	7.81	0.05*	24	132∼99	5	Cyclohexane (Not isolated)
Benzene	7.81	0.025	50	99∼70	6	Cyclohexane (Not isolated)
Toluene	9.21	0.05	25	99∼66	12	Methylcyclohexane (85)
Ethyl benzoate	15.0	0.05	24	98∼68	45	Ethyl hexahydrobenzoate (91)
Aniline	9.31	0.10*	23	75∼24	76	Cyclohexylamine (68) Dicyclohexylamine (20)
Aniline	9.31	0.05	50	80∼51	35	Cyclohexylamine (56) Dicyclohexylamine (29)
Phenol	9.41	0.05	32	99∼65	12	Cyclohexanol (85)
Acetophenone	12.0	0.05	27	100∼70	55	Cyclohexylmethylcarbinol (82) Ethylcyclohexane (6)
Pyridine	7.91	0.05	50	100∼71	20	Piperidine (Not isolated)

a) 50 ml. of acetic acid was used as solvent.

* The oxide was pre-reduced in the absence of the substrate.

the catalyst aniline gives a better yield of cyclohexylamine than with platinum oxide[4]. Phenol and acetophenone gave with good yields the corresponding saturated alcohols. Pyridine hydrogenates rather slowly at room temperature, but rapidly at 50°C. Thus, the high pressure hydrogenation with rhodium-platinum oxide is a very useful synthetic method. Its high acitivity at low temperatures may be advantageous in many selective hydrogenations. Further studies on the catalytic activity and selectivity of the rhodium-platinum oxide under high pressures are in progress.

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The Institute of Physical and
Chemical Research
Bunkyo-ku, Tokyo

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[4] With platinum oxide under similar conditions, cyclohexylamine and dicyclohexylamine were obtained in yields of 17 and 23% respectively (Ref. 3); cf. G. S. Hier and R. Adams, *Ber.*, **59**, 162 (1926).