Hydrogenation and Hydrogenolysis. VIII.[1] *The Ruthenium-catalyzed Hydrogenation of Aromatic Compounds Containing C–O Linkage to be Easily Hydrogenolyzed*

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In a series of papers[1,2] it has been shown that (3 : 1) or (7 : 3) rhodium-platinum oxide of Adams' type is a very effective catalyst for selective hydrogenation where one desires to avoid the hydrogenolysis of the C–O linkage. Similar results have also been reported in hydrogenation with 5% rhodium-on-alumina as the catalyst.[3-6]

Only a few examples of the use of ruthenium catalysts in the selective hydrogenation of this kind seem to have been described in the literature. Fairly good yields have been obtained in the hydrogenation of some phenyl-substituted α, ω-glycols,[7] *p*-aminoacetophenone[8] and benzaldehyde[9] to the corresponding saturated glycols or alcohols.

This paper will describe the general applicability of ruthenium dioxide catalyst to the selective hydrogenation of aromatic compounds containing C–O linkage to be easily hydrogenolyzed. This catalyst was also compared with rhodium or (7 : 3) rhodium-platinum oxide in some hydrogenations.

The ruthenium-catalyzed hydrogenation of the aromatic compounds listed in Table I was carried out at 95 to 100°C and under 80 to 100 kg./cm^2 of hydrogen pressure. Usually the use of a solvent was unnecessary, although a small amount of acetic acid was added to neutralize a trace of alkaline substances remaining in the catalyst. Under these conditions most hydrogenations proceed rather rapidly, and good yields of the corresponding saturated alcohols or ethers are obtained. For the successful hydrogenation of benzyl alcohol and benzaldehyde, it was necessary to use ethanol or water as the solvent; otherwise the rate decreased markedly during the hydrogenation. It should be noted that the hydrogenation of these compounds with rhodium or (7 : 3) rhodium-platinum oxide was unsuccessful, even in the presence of alcohol or water.[10] Platinum oxide gives a good yield of cyclohexylcarbinol in the hydrogenation of benzyl alcohol in ethanol containing a small amount of acetic acid,[11] but the rate of the hydrogenation is slow, even under high pressure.

The proporition of hydrogenolysis was somewhat greater with ruthenium dioxide than with rhodium or (7 : 3) rhodium-platinum oxide in the hydrogenation of phenyl ether, hydroquinone dimethyl ether and ethyl *p*-hydroxybenzoate. The probable cause of the higher selectivity of rhodium and (7 : 3) rhodium-platinum oxides over ruthenium dioxide is their use at lower temperature, the former catalysts being sufficiently active at that temperature. It may be explained on the basis of the same reasons that a somewhat larger quantity of *trans*-1, 4-dimethoxycyclohexane and ethyl *trans*-4-hydroxycyclohexane-1-carboxylate was obtained with ruthenium dioxide than with rhodium or (7 : 3) rhodium-platinum oxide.

Benzyl acetate, where the most extensive hydrogenolysis occurred among the compounds investigated, gave a 30% yield of hexahydrobenzyl acetate with ruthenium dioxide. This yield was better than those obtained with rhodium or (7 : 3) rhodium-platinum oxide, though the reaction temperature was higher for the ruthenium catalyst.

Experimental

Catalysts—Ruthenium dioxide was prepared according to the method of Pichler and Buffleb.[12]

Rhodium oxide and (7 : 3) rhodium-platinum

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1) Part VII of this series: S. Nishimura and H. Taguchi, This Bulletin, **36**, 353 (1963).

2) S. Nishimura et al., ibid., **33**, 566, 1356 (1960); **34**, 32, 1544 (1961); **36**, 318 (1963).

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

4) H. A. Smith and B. L. Stump, *J. Am. Chem. Soc.*, **83**, 2379 (1961).

5) J. H. Stocker, *J. Org. Chem.*, **27**, 2288 (1962).

6) I. A. Kage and R. S. Matthews, ibid., **28**, 325 (1963).

7) H. W. Arnold, U. S. Pat. 2555912 (1951) [*Chem. Abstr.*, **46**, 3074f (1952)].

8) M. Freifelder and G. R. Stone, *J. Org. Chem.*, **27**, 3568 (1962).

9) Y. Takagi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **57**, 105 (1973).

10) Cf. S. Nishimura, This Bulletin, **34**, 32 (1961); J. H. Stocker, Ref. 5.

11) S. Nishimura, This Bulletin, **32**, 1155 (1959).

12) H. Pichler and H. Buffleb, *Brennstoff-Chem.*, **21**, 257 (1940).

TABLE I. HYDROGENATION OF AROMATIC COMPOUNDS CONTAINING C-O LINKAGE TO BE EASILY HYDROGENOLYZED WITH RUTHENIUM, RHODIUM, AND (7 : 3) RHODIUM-PLATINUM CATALYSTS*

Compound	Catalyst	Solvent or additive, ml.	Temp. °C	Time for hydrogenation min.	% Product
Anisole	Ru oxide	10%AcOH, 0.5	80～ 82	10	89 Cyclohexyl methyl ether[a]
Hydroquinone dimethyl ether	Ru oxide	10%AcOH, 0.5	95～100	200	74 1, 4-Dimethoxycyclohexane[b] (81% cis, 19% trans)[c] 13 Cyclohexyl methyl ether
Hydroquinone dimethyl ether	Rh oxide	AcOH, 0.05	50～ 55	65	91 1, 4-Dimethoxycyclohexane[c] (77% cis, 23% trans) 9 Cyclohexy methyl ether[c] Cyclohexane (trace)[c]
Hydroquinone dimethyl ether	Rh oxide**	AcOH, 15	30～ 32	30	91 1, 4-Dimethoxycyclohexane[c] (85% cis, 15% trans) 9 Cyclohexyl methyl ether[c] Cyclohexane(trace)[c]
Hydroquinone dimethyl ether	(7 : 3)Rh-Pt oxide	AcOH, 15	30～ 33	15	92 1, 4-Dimethoxycyclohexane[c] (83% cis, 17% trans) 8 Cyclohexyl methyl ether[c] Cyclohexane(trace)[c]
Phenyl ether	Ru oxide	10%AcOH, 0.5	95～100	38	66 Cyclohexyl ether[d] 25 Cyclohexanol[e] (+Cyclohexane)
Phenyl ether	Rh oxide**	AcOH, ca. 2	35～ 37	85	84 Cyclohexyl ether[c] 16 Cyclohexanol[c] (+Cyclohexane)
Phenyl ether	(7 : 3)Rh-Pt oxide	AcOH, 0.05	35～ 40	55	87 Cyclohexyl ether[f] 8 Cyclohexanol[f] (+Cylohexane)
Ethyl *p*-hydroxybenzoate	Ru oxide	EtOH, 30 + 10%AcOH, 0.5	95～100	75	96 Ethyl 4-hydroxycyclohexane-1-carboxylate[c,g] (84% cis, 16% trans) 4 Ethyl cyclohexanecarboxylate[c]
Ethyl *p*-hydroxybenzoate	Rh oxide	EtOH, 15 + AcOH, 0.05	50～ 65	30	98 Ethyl 4-hydroxycyclohexane-1-carboxylate[c] (87% cis, 13% trans) 2 Ethyl cyclohexanecarboxylate[c]
Benzyl alcohol	Ru oxide	EtOH, 30 + 10%AcOH, 0.5	95～100	80	81 Cyclohexylcarbinol[h]
Benzaldehyde	Ru oxide	H_2O, 30 + 10%AcOH, 0.5	95～100	54	72 Cyclohexylcarbinol
Benzyl acetate	Ru oxide	10%AcOH, 0.5	95～100	44	30 Hexahydrobenzyl acetate[i] (+Methylcyclohexane)
Benzyl acetate	Rh oxide**	AcOH, ca. 2	30～ 32	80	18 Hexahydrobenzyl acetate[c] 82 Methylcyclohexane[c]
Benzyl acetate	(7 : 3)Rh-Pt oxide	AcOH, 0.05	30～ 35	50	20 Hexahydrobenzyl acetate[c] 80 Methylcyclohexane[c]
Benzyl ether	Ru oxide	10%AcOH, 0.5	95～100	125	85 Hexahydrobenzyl ether[j] 6 Cyclohexylcarbinol (+Methylcyclohexane)
Acetophenone	Ru oxide	10%AcOH, 0.5	95～100	7	90 1-Cyclohexylethanol[k]
Benzophenone	Ru oxide	10%AcOH, 0.5	95～100	22	Dicyclohexylcarbinol

* The substrate (0.1 mol.) was hydrogenated with 0.1 g. (as oxide) of the catalyst at 80 to 100 kg./cm² pressure of hydrogen.

** The oxide was pre-reduced for about one and a half hours in acetic acid at 40 to 45°C under the atmospheric pressure of hydrogen.

a) B. p. 131°C ; n_D^{20} 1.4342 b) B. p. 76～80°C/23 mmHg c) Analyzed by gas chromatography d) B. p. 122～123°C/23 mmHg ; n_D^{20} 1.4691 e) B. p. 73～74°C/23 mmHg ; n_D^{22} 1.4632 f) The yields obtained by distillation. Gas chromatography shows 90% of cyclohexyl ether and 9% of cyclohexanol. g) Ethyl 4-hydroxycyclohexane-1-carboxylate, b. p. 152～153°C/23 mmHg, n_D^{25} 1.4645, was obtained in 91% yield by distillation. h) B. p. 95～95.5°C/28 mmHg ; n_D^{25} 1.4615 i) B. p. 89°C/22mmHg ; n_D^{20} 1.4428 j) B. p. 153～154°C/23 mmHg ; n_D^{20} 1.4693 k) B. p. 96～97°C/30 mmHg ; n_D^{25} 1.4637 l) B. p. 167～168°C/30 mmHg ; m. p. 62～63°C.

oxide were prepared according to the procedure described previously.[13]

Hydrogenations. — All the hydrogenations were carried out in a 100 ml. bomb of an electro-magnetically-stirring type.

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[13] S. Nishimura, This Bulletin, **34**, 1544 (1961).