aqueous ethyl alcohol. The recrystallized product melted at 62–63°. The identification of the product was confirmed by conversion to dioxime, m.p. 184–186°, and mixture melting point with a known sample of the derivative. The pH of the aqueous solution after benzene extraction was 3.5. It contained active oxygen which was determined iodometrically. The amount of active oxygen found was equal to 73% of that which would be expected from the hydrogen peroxide formed by the decomposition of 0.028 mole of IV.

Preparation of 4,5,6,7-Dibenzo-1,2-dioxa-3,8-cyclooctanediol (IV).—Three grams of pure diphenaldehyde (m.p. 63°) was stirred with 160 g. of 15% aqueous hydrogen peroxide for 1 hr. at 25°. At the end of this time substantially all the solid was in solution. The mixture was left overnight. The voluminous white precipitate which formed was separated by filtration, washed with a small amount of water and dried in a vacuum oven at 35°. The product melted at 105–106°. It was insoluble or only very slightly soluble in water at 25° and less than 2% soluble in 95% ethyl alcohol at that temperature. The yield was 3.1 g., (90%). In addition to the results of infrared examination which showed the presence of hydroxyl groups and the absence of carbonyl groups, the product had the following evidence of constitution.

Anal. Calcd. for IV, $C_{14}H_{12}O_4$: C, 68.8; H, 4.9; hydroxyl, 13.9; active oxygen, 6.6. Found: C, 68.3; H, 4.9; hydroxyl, 13.1; active oxygen, 6.3.

Erratic yields of IV were obtained with samples of V which were not too highly purified. It was found to be of advantage to heat the sample of V to 95° in a vacuum oven prior to mixing with the hydrogen peroxide. High yields (up to 95%) of IV were obtained consistently with material so treated.

Alkaline Decomposition of IV.—One gram of IV was refluxed with 100 g. of 5% sodium hydroxide solution for 2 hr. The clear solution was cooled to 5° and acidified to pH 1 by the dropwise addition of dilute hydrochloric acid. The slurry was held at 5° for 2 hr., then filtered, washed thoroughly with water, and dried in vacuum. The product weighed 0.90 g. and was identified as VII by its m.p. 143.5–144.5°. The melting point was unchanged when the product was mixed with an authentic sample of VII. The yield was 96%.

Oxidation of Diphenaldehyde with Dilute Nitric Acid.—One hundred grams of crude V, m.p. 58–62°, was refluxed with 1 l. of 35% (by wt.) nitric acid for 1 hr. The reaction mixture was cooled and the solids separated by filtration. The product was washed with water and then reslurried with warm 5% sodium hydroxide solution, separated again, washed thoroughly with water, and dried. Yield of phenanthraquinone, m.p. 203–205° (lit.[14] m.p. 206.5–207.5°), was 72.7%. Acidification of the alkaline solution gave 22 g. (19.1%) of crude diphenic acid, m.p. 214–220°, improved to 229–230° by recrystallization from 90% aqueous methanol. The literature[15] gives 229° as the melting point of diphenic acid.

Acknowledgment.—The assistance of Robert Mainier, Analytical Section, Research Department, Koppers Company, Inc., who performed the spectroscopic analyses, is acknowledged with gratitude.

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[14] N. B. Lange, "Handbook of Chemistry," 10th Ed., McGraw Hill Book Co., Inc., 1961, p. 649.

[15] E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," 5th Printing, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 172.

Rhenium Catalysts. VI. Rhenium(IV) Oxide Hydrate[1]

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Excess zinc in acid solutions in the presence of air reduces perrhenate to a finely divided black substance characterized as a hydrated rhenium(IV) oxide, probably $ReO_2 \cdot 2.5H_2O$. A survey of its catalytic activity in the hydrogenation of a variety of organic substrates is presented with particular attention to the selectivity of hydrogenation observed.

As a part of a research program directed toward a survey of the catalytic activity of rhenium compounds it has been found that zinc, tin, and iron, particularly zinc, readily reduce perrhenate in acid solutions in the presence of air to a very finely divided, insoluble, black hydrated rhenium(IV) oxide. The oxide was characterized by elemental analysis for rhenium and oxygen, dehydration, and oxidation state determination. The data obtained best support the formulation, $ReO_2 \cdot 2.5H_2O$, but do not preclude small variations from this composition.

The hydrate is very stable, indefinitely resisting dehydration at 95° over phosphorus(V) oxide *in vacuo*, and only very slowly losing water at 250°; however, when the hydrated oxide was heated with benzene at 250° under hydrogenation conditions, the recovered compound has the correct analysis for the anhydrous rhenium(IV) oxide, ReO_2. A small amount of water accompanied it as a co-product.

Young and Irvine[3] have reported the reduction of perrhenate with zinc and cadmium in hydrochloric acid solutions in the absence of air. They report the formation of $Re_2O \cdot 2H_2O$, using zinc as the reducing agent, and $ReO \cdot H_2O$, using cadmium, accompanied in either case by considerably larger amounts of rhenium(IV) not further characterized.

It has now been found that this hydrated rhenium(IV) oxide has activity as a hydrogenation catalyst. While this activity is much less than that of nickel or platinum catalysts in promoting the reduction of aromatic, olefin, carbonyl, and nitro groups, it is, on the other hand, much more effective than the platinum catalyst in promoting the reduction of the carboxylic acid function. This leads to a potentially valuable selectivity of reduction. Other rhenium oxides share this valuable property in varying degrees. Very few other elements show this characteristic in any degree.[4]

Table I summarizes the kind of results obtained in the hydrogenation of a variety of organic compounds using the hydrated rhenium(IV) oxide catalyst. Examples include compounds in which the olefin, carbonyl, nitro, and carboxyl moieties are represented, each alone, and in all but one of the possible binary combinations.

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[1] Support by the U. S. Air Force through its Office of Scientific Research, contract AF 18(600)-1164, is gratefully acknowledged.

[2] This paper is based on a portion of a thesis submitted by T. G. Selin (1957) in partial fulfillment of the requirements for the M.S. degree.

[3] R. C. Young and J. W. Irvine, Jr., *J. Am. Chem. Soc.*, **59**, 2648 (1937).

[4] *Cf.* papers III, VII, and VIII in this series: H. S. Broadbent, G. C. Shaw, W. J. Bartley, and J. H. Johnson, *J. Org. Chem.*, **24**, 1847 (1959); H. S. Broadbent and W. J. Bartley, *ibid.*, **28**, 2345 (1963); H. S. Broadbent and D. W. Seegmiller, *ibid.*, **28**, 2347 (1963).

TABLE I

HYDROGENATIONS USING $ReO_2 \cdot 2.5H_2O$ AS CATALYST[a]

No.	Substrate	Solvent	Temp., °C.	Time, hr.	Product[b]	Yield, %
1	Styrene	Ethanol	94	5	Ethylbenzene	100
2	1-Hexene	None	154	2	Hexane	100
3	Cyclohexene	None	132	6	Cyclohexane	100
4	2-Propyn-1-ol	None	163	12	2-Propen-1-ol	40
					Propanol	19
5	2-Butanone	None	100	4	2-Butanol	100
6	Cyclohexanone	None	115	12	Cyclohexanol	100
7	Cycloheptanone	None	167	6	Cycloheptanol	45
8	Acetophenone	None	143	8	Methylphenylcarbinol	64
					Ethylbenzene	29
9	5-Hexen-2-one	None	166	6	2-Hexanol	100
10	5-Hexen-2-one	None	104	6	2-Hexanone	91
					2-Hexanol	9
11	2-Allylcyclohexanone	None	168	10	2-Propylcyclohexanone	72
12	Crotonaldehyde	Ethanol	148	8	Butanol	100
13	Nitrobenzene	Ethanol	157	25	Aniline	45
14	*m*-Nitrostyrene	Ethanol	137	6	*m*-Aminostyrene	17
15	*m*-Nitroacetophenone	Ethanol	185	14	*m*-Aminoacetophenone	34
16	Acetic acid	None	156	24	Ethanol	50
					Ethyl acetate	50
17	Phenylacetic acid	Pet. ether	195	14	Phenethyl alcohol	42
					Phenethyl phenylacetate	58
18	Crotonic acid	Pet. ether	188	7	Butyl bytyrate	68
					Butyric acid	26
					Butyl alcohol	6
19	Vinylacetic acid	Pet. ether	161	12	Butyric acid	100
20	Maleic acid	Pet. ether	105	8	Succinic acid	100
21	Undecylenic acid	None	179	16	Undecanoic acid	40
					Undecanol	6
					Undecyl undecanoate	54
22	Levulinic acid	None	152	12	γ-Valerolactone	100
23	Benzene	None	177	14	Cyclohexane	100
24	Pyridine	None	230	22	Piperidine	38

[a] In each run, 0.10 g. of catalyst was used in the hydrogenation of 0.10 mole of substrate. [b] Yields are based on the crude recovered product. The balance was recovered starting material.

Examples of the aromatic and acetylenic moieties are also given. The olefinic bond is reduced more readily than the carbonyl group in the same compound (**10**, **11**); likewise the olefinic group is more readily reduced than the carboxyl group (**18**–**21**); and the carbonyl group is reduced more readily than the carboxyl group in the same compound (**22**).

It will be observed that olefins and ketones are subject to hydrogenation under conditions as mild or even milder than those required for the reduction of the nitro group (*cf.* **1**–**12** *vs.* **13**–**15**). Yet, when both nitro and olefinic groups (**14**) or nitro and carbonyl groups (**15**) are present in the same molecule, the reduction of only the nitro group occurs to the complete exclusion of concomitant hydrogenation of the other group.

Finally, attention is called particularly to the reduction of phenylacetic acid (**17**). The carboxyl group is hydrogenated to the alcohol function with complete selectivity, the aromatic ring remaining entirely intact.

Experimental

Hydrated Rhenium(IV) Oxide Catalyst. A. Preparation.—Ammonium perrhenate (Kennecott Copper Co., Inc.), 1.20 g., dissolved in 150 ml. of water, and an excess of zinc (granular, previously treated with dilute acid and thoroughly washed to ensure clean surfaces), 5–10 g., were vigorously stirred in a flask while 64 ml. of 3 *N* sulfuric acid was slowly added dropwise over a period of several hours. The black suspension of finely divided rhenium oxide was periodically decanted from the zinc, centrifuged, and the supernatant solution returned to the reaction flask. At the completion of the reaction the combined rhenium oxide residues were washed by suspension in distilled water followed by centrifugation until the washings were negative to the barium chloride test for sulfate ion. Then the residues were similarly washed with ethanol and stored under ethanol. The conversion of perrhenate to the insoluble oxide varied from 60 to 100% as determined by analysis of an aliquot of the original supernatant reaction solution. If an excess of zinc was maintained in the reaction flask, the reduction was quantitative. At times this required the addition of more zinc during the progress of the reaction. If the acid was added all at once, rather than dropwise, the rhenium oxide coated the zinc particles stopping the reduction at an early stage and also preventing the isolation of a zinc-free product.

B. Analysis for Rhenium.—The usual technique of dissolving the rhenium compound in ammoniacal hydrogen peroxide was not very effective. The following technique was used in preparing the sample for analysis. An aliquot of the catalyst suspension, estimated to contain 50-mg. solid, was transferred to a small screw-cap vial, dried for at least 14 hr. at 95°–110° *in vacuo* over phosphorus(V) oxide, closed under an atmosphere of dry nitrogen, and weighed. To dissolve the sample, it was heated in the tightly closed vial with five drops of water and 2–4 drops of concentrated nitric acid until only a flocculent, brownish precipitate remained in the vial. The sample was then transferred to a 150-ml. beaker and heated with a few milliliters of ammoniacal hydrogen peroxide until only a clear solution remained and all the hydrogen peroxide had decomposed. Perrhenate in solution was then determined in standard fashion as the tetraphenylarsonium salt.[5]

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[5] H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.*, **11**, 305 (1939).

C. **Analysis for Oxygen**.—The catalyst prepared and dried as described before was weighed (25–50-mg. samples) into small porcelain boats (Coors D-19) and heated for 30 min. at 600° in a slow stream of hydrogen in a microcombustion furnace, collecting the evolved water in a Pregl water absorption tube containing anhydrous magnesium perchlorate.

D. **Oxidation State**.—Samples (*ca.* 250 mg.) of the catalyst were prepared and dried as described before in 20-ml. screw-cap vials, then 250-mg. portions of potassium dichromate were weighed in with the samples, and 2–5-ml. portions of dilute sulfuric acid were added. The tightly closed vials were heated on the steam plate until the solid dissolved; then the contents were transferred to 250-ml. erlenmeyer flasks, treated with excess potassium iodide, and back-titrated to a starch end point with 0.1 *N* sodium thiosulfate.

Anal. Calcd. for $ReO_2 \cdot 2.5H_2O$: Re, 70.7; O, 28.0; change in oxidation no. [Re(IV) → Re(VII)], 3. Found: Re, 71.1; O, 28.0; change in oxidation no., 2.98. The rhenium value represents the average of thirteen determinations with a mean deviation of 0.4%; the oxygen value is the average of seven determinations with a mean deviation of 0.6%; and the oxidation state is the average of three determinations with a mean deviation of 0.05. Qualitative tests for zinc and sulfur were negative.

A sample of the rhenium oxide was first used to catalyze the hydrogenation of benzene at 250°, filtered off, and vacuum dried at 95° over phosphorus(V) oxide for several hours. A droplet of water immiscible with the benzene–cyclohexane mixture was found in the reactor in which the hydrogenation was run. This rhenium oxide sample was analyzed for rhenium.

Anal. Calcd. for ReO_2: Re, 85.3. Found: Re, 86.3, 86.4.

Hydrogenation Procedure.—The hydrogenation apparatus was a Parr Instrument Co. 500-ml. reactor with a fixed rocking rate of 36 cycles/min. The substrate,[6] 0.1 mole, an aliquot of the suspended catalyst equivalent to 0.1 g., and the solvent,[6] if any, were weighed into a tared glass liner and placed in the reactor. After flushing and charging the reactor to 200 atm. with hydrogen, it was tested for leaks and then set in motion. If reaction did not occur at a particular temperature, rocking was stopped and the reactor was brought to a new temperature 30–40° higher and rocking resumed. In this way, roughly minimal reaction conditions were achieved for each substrate.

The reaction products were analyzed by refractive indices (binary systems only), distillation, and especially by gas chromatography using silicone, polypropylene glycol, Carbowax, and/or dinonyl phthalate coated columns. Subsequent identification of the separated components was made by melting point, boiling point, and/or refractive index.

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[6] Organic substrates and solvents were of Eastman White Label grade or equivalent. No special purification was attempted or desired since a survey of the catalytic activity of the rhenium oxide was desired under the conditions generally employed by the practicing synthetic organic chemist.

Rhenium Catalysts. VII. Rhenium(VI) Oxide[1]

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Rhenium(VI) oxide is a very efficient catalyst for the hydrogenation of carboxylic acids and carboxamides, being comparable to the rhenium(VII) oxide which is the most efficient catalyst for these purposes yet reported. The former oxide, which can be very easily and simply made from the latter, is nonhygroscopic and stable in air, thus enjoying considerable advantage in handling over the commercially available higher oxide.

Rhenium(VI) oxide reduced *in situ* has been found to be an excellent catalyst for the liquid-phase hydrogenation of a variety of organic substrates, particularly carboxylic acids and carboxamides, for which it is comparable to rhenium(VII) oxide reduced *in situ*,[3] which is the most effective hydrogenation catalyst for these purposes heretofore reported.

The rhenium(VI) oxide used in this study was prepared by a modification of the method of Nechamkin, *et al.*,[4] in which the sometimes difficult isolation of an intermediate crystalline complex of rhenium(VII) oxide and *p*-dioxane under anhydrous conditions was found to be unnecessary. Excellent yields were obtained, even in the presence of water, from both *p*-dioxane and tetrahydropyran. the latter being the reagent of choice.[5]

Rhenium(VI) oxide occurs as maroon-red crystals, stable in air below 100°, inert to water, dilute alkali, and most agents of nonoxidizing or reducing character. It is nonhygroscopic, which makes it more convenient to store and handle than the extremely hygroscopic rhenium(VII) oxide.

The nature and composition of the actual catalytic material resulting from the hydrogenation *in situ* of the rhenium(VI) oxide was not conclusively determined.[6] Analyses indicated that while lower oxides of rhenium predominate, some of the initial oxide remains unchanged. Elementary analyses and oxidation state determinations gave variable results.

A representative selection of hydrogenations carried out with ReO_3, *in situ*, as the catalyst are shown in Table I. In common with the Re_2O_7 catalyst, esters (**10, 11**), ketones (**18–20**), aldehydes (**21–23**), and olefins (**13–15**) can be readily hydrogenated although considerably more rigorous conditions are required than for nickel or platinum metal catalysts or most other rhenium catalysts (*cf.* previous papers in this series). Nitro compounds (**23–26**), ordinarily the most easily reduced of all compounds, required the most drastic hydrogenation conditions with ReO_3 catalyst. Aromatic rings (**16, 17**) are exceptionally resistant to hydrogenation in marked contrast to their ease of hydrogenation with the rhenium(VII) oxide–tetrahydropyran complex previously reported,[5] which is actually a precursor to the preparation of ReO_3. This phenomenon permits the selective reduction of even the carboxylic acid group without an accompanying hydrogenation of the aromatic ring (**9, 22, 23, 30, 31**).

Various carboxylic acids (**1–9**) except formic acid, on the other hand, are easily reduced to good yields of the corresponding alcohols at 145–165°. Interestingly, contrary to the effect of all other types of catalysts re-

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[1] Support by the U. S. Air Force through its Office of Scientific Research, contract AF18(600)-1164, is gratefully acknowledged.

[2] This paper is based on a thesis submitted by W. J. Bartley (1958) in partial fulfillment of the requirements for the M.S. degree.

[3] H. S. Broadbent, G. C. Shaw, W. J. Bartley, and J. H. Johnson, *J. Org. Chem.*, **24**, 1847 (1959).

[4] H. Nechamkin, A. N. Kurtz, and C. F. Hiskey, *J. Am. Chem. Soc.*, **73**, 2828 (1951); H. Nechamkin and C. F. Hiskey, *Inorg. Syn.*, **3**, 186 (1950).

[5] *Cf.* H. S. Broadbent and J. H. Johnson, *J. Org. Chem.*, **27**, 4402 (1962).

[6] *Cf.* ref. 3, Paper III in this series.