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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Received August 27, 1962

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.

TABLE I

HYDROGENATIONS CATALYZED BY ReO_3 REDUCED *in situ*

No.	Substrate	Solvent	Av. temp., °C.	Time, hr.	Product[a]	Yield, %
1	Formic acid	Water	166	4	No reduction	
2	Acetic acid	None	166	5	Ethyl alcohol	67
					Ethyl acetate	33
3	Butyric acid	Cyclohexane	144	10	*n*-Butyl alcohol	100
4	Isobutyric acid	Water	146	10	Isobutyl alcohol	90
					Isobutyl isobutyrate	10
5	Crotonic acid	Water	146	10	*n*-Butyl alcohol	80
					n-Butyl butyrate	20
6	Valeric acid	None	145	11	*n*-Amyl alcohol	75
					n-Amyl valerate	25
7	Caprylic acid	Cyclohexane	144	7	*n*-Octyl alcohol	100
8	Undecylenic acid	Water	156	12	*n*-Undecyl alcohol	100
9	Benzoic acid	Water	165	10	Benzyl alcohol	43
10	Ethyl acetate	None	175	50	Ethyl alcohol	84
11	*n*-Butyl butyrate	None	218	28	*n*-Butyl alcohol	85
12	Ethyl benzoate	Cyclohexane	237	80	Benzyl alcohol[b]	93
13	1-Hexene	None	95	15	Hexane	100
14	Cyclohexene	None	131	4	Cyclohexane	100
15	Styrene	Cyclohexane	135	4	Ethylbenzene	100
16	Benzene	None	240	4	Benzene	100
17	Pyridine	None	225	26	Piperidine	48
18	3-Pentanone	None	161	1	3-Pentanol	100
19	2,3-Butanedione	Ethanol	204	10	2,3-Butanediol	73
20	Cyclohexanone	None	123	7	Cyclohexanol	47
21	Crotonaldehyde	Cyclohexane	147	16	*n*-Butyl alcohol	100
22	Benzaldehyde	Cyclohexane	124	20	Benzyl alcohol	88
23	*m*-Nitrobenzaldehyde	Cyclohexane	181	5	*m*-Aminobenzyl alcohol[c]	23
24	2-Nitropropane	None	227	13	2-Aminopropane[c]	46
25	Nitrocyclohexane	None	234	36	Cyclohexylamine[c]	68
26	Nitrobenzene	None	226	25	Aniline	100
27	Hydrazobenzene	Cyclohexane	185	33	Aniline	100
28	Azobenzene	Cyclohexane	195	15	Aniline[c]	96
29	Acetamide	Cyclohexane	200	18	Ethylamine	88
30	Benzamide	Ethanol	220	49	Benzylamine	69
					Toluene	10
31	Acetanilide	Cyclohexane	185	31	N-Ethylaniline	71
					Aniline	29

[a] The unaccounted for balance, if any, is unchanged starting material unless yields are based on recovered product. [b] Exclusive of ethanol. [c] The balance of the material was unidentified tarry residue.

ported, esters (**10–12**) require more strenuous reducing conditions than the corresponding acids.

It is especially noteworthy that benzoic acid, ethyl benzoate, benzaldehyde, and *m*-nitrobenzaldehyde (**9**, **12**, **22**, **23**) are reduced to the corresponding aromatic carbinols instead of suffering hydrogenolysis to the toluenes which result from most catalytic hydrogenations.

Amides (**29–31**) are hydrogenated at 185–200° in fair to good yields to the corresponding alkylamines accompanied by only minor amounts of the hydrogenolysis products.

Experimental

Preparation of Catalysts.—One gram of rhenium(VII) oxide was weighed out and added directly to 10–25 ml. of *p*-dioxane or tetrahydropyran in a 50-ml. beaker. After gentle warming to produce a colorless to dark green solution, the excess solvent was removed under reduced pressure at room temperature leaving a tacky, black, tarry complex. Upon careful heating to *ca.* 145°, the complex decomposed into gaseous products and a pure, red, crystalline residue of rhenium(VI) oxide. The residue was finely powdered and stored dry in an ordinary screw-cap vial. In 13 preparations yields varied from 84 to 98% with an average of 95%.

Analysis of Catalyst.—Analyses for rhenium content and oxidation state of the catalyst were carried out as described in the previous paper in this series.[7]

Anal. Calcd. for ReO_3: Re, 79.51; change in oxidation no. (VI → VII), 1.00. Found: Re, 77.15, 77.26, 76.91; change in oxidation no. (VI → VII), 1.06 (average of several determinations).

Hydrogenation Procedure.—The apparatus used was either a Pressure Products, Inc., 330-ml. "Pendaclave" shaking reactor operated at 44 cycles/min. or an Aminco 500-ml. rocking reactor rocking at 36 cycles/min., both equipped with glass liner and Leeds & Northrup X_1-X_2 recorder for continuous, simultaneous recording of both temperature (iron-constantan thermocouple) and pressure (Baldwin strain gage). There was no significant difference in these experiments between the two reactors.

The catalyst (0.20 g.), 15 g. of substrate, and solvent, if any, (usually 25 ml.) were weighed into the tared liner and introduced into the reactor, which was charged with hydrogen to 205 atm. and agitated for 0.5 hr. at room temperature to ensure the absence of leaks. (Previous experience had shown that no hydrogenation would occur at room temperature.) Then the reactor temperature was increased by 25–50° increments (The reactor was not shaken until temperature equilibrium was established at each new plateau.) until the rate of hydrogenation became appreciable at which time the temperature was held constant and the reaction continued until all hydrogen absorption

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(7) H. S. Broadbent and T. G. Selin, *J. Org. Chem.*, **28**, 2343 (1963).

had ceased as evidenced on the pressure recording. In this way minimal (rather than optimum) conditions for practical hydrogenation were obtained. Doubtless many hydrogenations were substantially complete in less time than actually recorded.

After completion of the hydrogenation, the reactor was cooled, vented, and the reaction product analyzed by refractive index (for binary mixtures only) and gas chromatography (using silicone, polypropylene glycol, Carbowax, diglycerol, and di-*n*-decyl phthalate coated columns depending on the system being chromatographed).

Rhenium Catalysts. VIII. Rhenium(II) Oxide Dihydrate from Perrhenate *via* Alkali Metal–Amine Reductions[1,2]

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Ammonium perrhenate and rhenium(VII) oxide (but not potassium perrhenate) are reduced by sodium or lithium (but not potassium) in liquid ammonia or lithium in ethylamine to black, insoluble rhenium(II) oxide dihydrate ($ReO \cdot 2H_2O$), a new compound of rhenium, stable to dehydration at 100° over phosphorus(V) oxide. This rhenium oxide is a catalyst for the hydrogenation of many organic compounds, being particularly efficient for the hydrogenation of the carboxylic acid function. Some interesting examples of selective hydrogenation are reported.

There has been much interest in recent years in the reduction of both organic and inorganic substances by solutions of alkali metals in liquid ammonia or low molecular weight aliphatic amines.[4] While such solutions have great reducing power, reaction rates and solubility relationships are often greater factors than reduction potentials in determining reaction products. For instance, potassium halides in liquid ammonia are reduced to potassium metal by calcium with attendant precipitation of the insoluble calcium halides.[5] On the other hand, iron(II) oxide is incompletely reduced by alkali metals in liquid ammonia because the oxide or its reduction products so strongly catalyzes the competing reaction leading to the formation of the alkali metal amide.[6] Many similar examples have been found.[5,7]

The products of reduction of inorganic compounds by alkali metals in liquid ammonia or amines include the free metals, intermetallic compounds, lower valent oxides, halides, and other salts, amides, and hydroxides, often as their complex amines.[7] The products to be expected in any given reduction cannot be reliably predicted.

Watt and co-workers have examined the catalytic activity in low temperature hydrogenation of olefins, principally allyl alcohol, and of nitrobenzene by iron,[8] cobalt,[9] nickel,[10] iridium,[11] platinum,[12] ruthenium,[13] rhodium,[13] and palladium[13] obtained by the reduction of some of their compounds with potassium in liquid ammonia.

As a part of our program investigating the catalytic properties of rhenium and its compound, we have examined the reduction of rhenium(VII) compounds with sodium, potassium, and lithium in liquid ammonia and ethylamine.

Ammonium perrhenate and rhenium(VII) oxide are readily reduced by sodium in liquid ammonia and by lithium in liquid ammonia or ethylamine to the rhenium(II) state. After removal of co-products a new compound, rhenium(II) oxide dihydrate, $ReO \cdot 2H_2O$, stable at 100° over phosphorus(V) oxide *in vacuo* was isolated. It is a black, very finely divided powder. Suspensions in ethanol, in which it was stored for use, readily settled out, but suspensions in water required over twenty-four hours to settle out completely. It was characterized by elemental analysis and oxidimetry. Flame photometry and Kjeldahl analysis denoted the complete absence of alkali metals and nitrogen.

A related compound, rhenium(II) oxide monohydrate has been reported by the reduction of perrhenate with cadmium in hydrochloric acid as the acid insoluble portion of the product along with a much larger amount of an acid soluble tetracovalent compound of rhenium.[14] Russian workers have recently reported the hydrolysis of $HReCl_4 \cdot 2H_2O$ to a new substance described as $H_2Re(OH)_4$.[15] This substance may be regarded as a rhenium(II) oxide trihydrate.

Our rhenium(II) oxide dihydrate catalyzes the hydrogenation of a wide variety of organic substrates with unusual selectivity as detailed in the accompanying Tables. This rhenium oxide is accompanied in the crude state by relatively large amounts of alkali metal amide, the production of which is catalyzed by the solid rhenium oxide. These contaminants, which have a very adverse affect on the catalytic activity of the rhenium(II) oxide, were removed by extraction with dilute hydrochloric acid followed by extraction with ethanol.

The activity of the catalyst was essentially independ-

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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) Paper VII in this series, H. S. Broadbent, and W. J. Bartley, *J. Org. Chem.*, **28**, 2345 (1963).

(3) This paper is based on a thesis submitted by D. W. Seegmiller (1957) in partial fulfillment of the requirements for the M.S. degree.

(4) Examples of recent reviews: A. J. Birch and H. Smith, *Quart. Rev.* (London), **12**, 17 (1958); G. W. A. Fowles and D. Nicholls, *ibid.*, **16**, 19 (1962).

(5) C. A. Kraus, *Chem. Rev.*, **8**, 251 (1931).

(6) J. E. Moore and G. W. Watt, *J. Am. Chem. Soc.*, **64**, 2775 (1942).

(7) G. W. Watt, *Chem. Rev.*, **46**, 289 (1950).

(8) G. W. Watt and W. A. Jenkins, Jr., *J. Am. Chem. Soc.*, **73**, 3275 (1951).

(9) G. W. Watt and C. W. Keenan, *ibid.*, **74**, 2048 (1952).

(10) G. W. Watt and D. D. Davies, *ibid.*, **70**, 3753 (1948); G. W. Watt, W. F. Roper, and S. D. Parker, *ibid.*, **73**, 5791 (1951).

(11) G. W. Watt and P. I. Mayfield, *ibid.*, **75**, 6178 (1953).

(12) G. W. Watt, M. T. Walling, Jr., and P. I. Mayfield, *ibid.*, **75**, 6175 (1953).

(13) G. W. Watt, A. Broodo, W. A. Jenkins, and S. G. Parker, *ibid.*, **76**, 5989 (1954).

(14) R. C. Young and J. W. Irvine, Jr., *ibid.*, **59**, 2648 (1937).

(15) A. S. Kotel'nikova and V. G. Tronev, *Zh. Neorgan. Khim.*, **3**, 1008 1958); *Chem. Abstr.*, **52**, 16970 (1958).