Anal. Calcd. for $C_{14}H_{18}N_2O_4$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.11; H, 6.36; N, 10.25.

Deaminations. a. A solution of 0.129 g. of *trans*-2-aminocycloheptanol in 1.0 ml. of glacial acetic acid and 2.0 ml. of water was cooled in salt-ice bath. To this cooled solution was added a chilled solution of 1.4 g. of sodium nitrite in 3.0 ml. of water, and the solution allowed to stand in the cold for 30 min. The reaction was made basic with 20% sodium hydroxide solution, and extracted with ether. The ethereal extracts were dried and the solvent removed on the steam bath through a short column, affording 0.106 g. (96%) of yellow oil. This oil was treated with 2,4-dinitrophenylhydrazine reagent to give a yellow powder, m.p. 165–169°. Recrystallization from ethanol–ethyl acetate gave yellow-orange crystals, m.p. 170–172°. A mixed melting point with the dinitrophenylhydrazone of hexahydrobenzaldehyde[14] showed no depression.

b. A solution of 0.135 g. of *cis*-2-aminocycloheptanol in 3.0 ml. of water was cooled in an ice bath. To this solution was added a cold solution of 1.0 g. of sodium nitrite in 3.0 ml. of water and 1.0 ml. of glacial acetic acid. The reaction mixture was allowed to stand in the cold 30 min., made basic with dilute sodium hydroxide, and extracted with two portions of ether. The solvent was removed on the steam bath to give 0.073 g. (62%) of oil which was converted to the 2,4-dinitrophenylhydrazone, obtained as a yellow powder, m.p. 142–145°. Recrystallization from ethanol gave yellow crystals m.p. 147–148°, undepressed on mixing with an authentic sample of cycloheptanone-2,4-dinitrophenylhydrazone.[15] Treatment of 0.073 g. of the crude product with dimedone solution gave 0.039 g. of the dimedone derivative of cyclohexylmethanal. A blank run on pure cyclohexylmethanal indicated 50% recovery of the aldehyde. Consequently the deamination mixture contained 18% of cyclohexylmethanal.

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ATLANTA, GA.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BRIGHAM YOUNG UNIVERSITY]

Rhenium and Its Compounds as Hydrogenation Catalysts.
III. Rhenium Heptoxide[1,2,3]

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The hydrogenation catalytic activity of some rhenium "blacks" obtained by the reduction of commercially available rhenium heptoxide has been examined. The catalysts were prepared by hydrogenation of the heptoxide in a solvent prior to the addition of the reducible substrate (*ex situ*), or in the presence of the substrate subsequently and/or simultaneously being reduced (*in situ*). These rhenium "blacks" have been shown to be easily the most effective catalysts yet reported for the hydrogenation of the carboxylic acids to alcohols. They promote this conversion with a wide variety of acids at 150–250° (usually 160°)/*ca.* 200 atm. in a few hours, giving excellent yields of alcohols accompanied occasionally by ester by-product. Unreduced acid rarely survives. They are also unusually effective in the hydrogenation of amides. On the other hand, these catalysts show only moderate but definite activity toward many of the common organic functions reducible through the agency of platinum or nickel catalysts.

Relatively little work on the catalytic properties of rhenium metal in hydrogenation has been reported[5] and none on its oxides. Schmidt[6] reports that rhenium displays average activity as a hydrogenation catalyst being less active than platinum, palladium, or nickel. A colloidal rhenium sol was reported to be effective in reducing the ethylenic bonds of maleic and cinnamic acids with very high ratios of rhenium to substrates[7] Rhenium supported on unglazed porcelain by reducing the ammonium perrhenate-soaked carrier in a hydrogen stream at 500–600° was ineffective toward maleic acid and cyclohexene at 20° at 1 atm., but at 350° cyclohexene was reduced and benzene slowly decomposed stepwise to methane.[8] Nitric oxide was re-

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[1] Part I of this series: H. S. Broadbent, L. H. Slaugh, and N. L. Jarvis. "Rhenium Sulfides as Liquid-Phase Hydrogenation Catalysts. A Comparison with Molybdenum Sulfide and Cobalt Polysulfide," *J. Am. Chem. Soc.*, **76**, 1519 (1954).

[2] This research was supported by Contract No. AF 18 (600)-1164 with the United States Air Force through the Office of Scientific Research of the Air Research and Development Command. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[3] Presented in part at the 131st meeting of the American Chemical Society in Miami, Florida, April 11, 1957.

[4] This paper is based largely upon theses submitted by Mr. Campbell (1955) and by Mr. Bartley (1958) in partial fulfillment of the requirements for the degree of Master of Science, Brigham Young University.

[5] For a complete review to 1940 see "Gmelin's Handbuch der anorganischen Chemie," 8th Ed., Verlag Chemie, Berlin, 1941, No. 70, pp. 37–40. Since that time very little has been reported.

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[7] C. Zenghelis and K. Stathi, *Compt. rend.*, **209**, 797 (1939); *Chem. Abstr.*, **34**, 669 (1940).

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duced to ammonia and nitrogen at 400° and nitrobenzene to aniline at 250°. The same type catalyst hydrogenated ethylene at 300°[9] and unsaturated hydrocarbons of at least three carbon atoms "at sufficiently high temperatures."[10] A quartz sand supported rhenium catalyst reduced carbon monoxide to methane about as well as osmium.[11] Hydrogenation as well as desulfurization of certain oxygen containing compounds as phenols, cresols etc. is reported either by rhenium alone or with other catalysts.[12] The nitrogen-hydrogen(deuterium)-ammonia system over rhenium[13] and rhenium-iron mixtures[14] has been studied.

A number of catalytic hydrogenations of carboxylic acids to alcohols using non-rhenium catalysts have been reported under a variety of conditions—all of them strenuous. Representative among them are the use of copper catalysts at 300–400° above 200 atms. pressure,[15] of copper-chromium catalysts (for the higher acids) at near 300° and 250–300 atm.,[15,16] of copper-cadmium catalysts at 280° and 130 atm.,[17] of copper-cobalt-nickel promoted catalysts at 120–300° and 30–400 atm.,[18] of ferrous metals modified with various non-ferrous chromites at 200–400° and 100–200 atm.,[19] and most recently, after this work was in progress, of ruthenium dioxide at 150° and 500–1000 atm.[20] Cadmium-nickel salts of the carboxylic acids have been shown to yield alcohols using copper chromite at 240° and 235 atm. if the system is scrupulously dry.[21] The self-catalyzed reduction of certain acid salts if reported at 240–400° at above 135 atm.[22] The reduction of acids to esters by a modified cobalt catalyst is likewise reported.[23] An interesting transhydrogenation of acids to aldehydes using formic acid and titanium dioxide catalyst has been recorded,[24] but a subsequent investigation was unable to confirm it.[25]

EXPERIMENTAL

Catalysts. Rhenium heptoxide. This compound was used as purchased from A. D. Melaven, Department of Chemistry, University of Tennessee, Knoxville, Tennessee. Great care was employed to retain dryness in transfer because of its extreme hygroscopicity, comparable to phosphorus pentoxide.

Ex Situ reduction of rhenium heptoxide to rhenium black without extrinsic catalysis. The finely powdered heptoxide (1 g.) was suspended or dissolved in ca. 50 ml. of the appropriate solvent (anhy. ethanol, anhy. *p*-dioxane, glac. acetic acid or water) and hydrogenated at an initial hydrogen pressure of 136 atm. (2000 p.s.i.) in a glass-lined shaker tube under conditions designed to give approximately minimal times and temperatures of reduction. (*Cf.* Part I of this series[1] for the general procedure of determining minimal conditions.) The conditions of preparation of the catalysts given in Table I are representative of a large number of individual runs. While the conditions for preparation in different solvents varied greatly, of course, duplicability for a given solvent was good. *With extrinsic catalysis.* The foregoing procedure was varied by the addition of traces of platinum dioxide, 5% rhodium on alumina, 5% ruthenium on carbon, palladous oxide or previously prepared rhenium black, in amounts equivalent to 0.01 times the formal concentration of rhenium heptoxide. These reductions were usually performed in a glass shaker bottle at low pressures and temperatures (4 atm., 60°) rather than at higher pressures and temperatures. Table II gives representative conditions for reduction of the heptoxide to the catalyst.

The finely divided rhenium blacks were isolated by filtration or centrifugation, then washed several times and stored until ready for use under the solvent to be used in subsequent reductions with the catalyst. Occasionally the catalyst was dried *in vacuo* and stored under nitrogen. So long as the catalyst remained out of contact with oxygen its activity was unimpaired. In many cases where *in situ* hydrogenation conditions were observed the presence of small amounts of oxygen was not deleterious.

Completeness of reduction was determined by analysis of the filtrate, using nitron, tetraphenylarsonium chloride, or electrolysis. In most cases reduction was complete.

Hydrogenation procedures. Both Aminco 550 ml. and Parr 1000 ml. standard rocking type reactors were used. Both operated at fixed speeds of 36 rocking cycles per minute. In later experiments a Pressure Products Industries 300 ml. shaking type "Pendaclave" reactor having a variable rate of shaking was also used. It was operated at 45 cycles/min. at full amplitude. Faster agitation did not seem to appreciably increase the rate of hydrogenation within the range of conditions used. Pyrex glass liners were used in every case. Temperature and pressure changes were recorded simultaneously throughout the course of the reactions *via* Bourdon tube, Baldwin fluid pressure cell, and

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TABLE I

Conditions for the *ex situ* Reduction of Rhenium Heptoxide to Rhenium "Blacks" by Hydrogenation in Various Solvents *Without* Extrinsic Catalysis

Run No.	Solvent[a]	Avg. Temp. (°C.)	Avg. Pressure (atm.)	Time (hr.)	Comment[b]
9	*p*-Dioxane	120	167	2	Black, coarse particles[c]
3	Ethanol	220	211	1	Black, coarse particles[d]
21	Acetic acid	165	153	1	Black, very finely divided, partly colloidal[e]
25	Water	140	177	2	Shiny flakes[f]

[a] Rhenium heptoxide was in the powdered state. The approximate solubilities by weight in these solvents are as follows: *p*-dioxane, 5%; ethanol, 10%; acetic acid and water, very large. [b] Reduction was complete in every case. [c] Analysis: Re, 97.4, 97.5, 97.0%. [d] Analysis: Re, 102.0, 102.5%. These values are representative of many. The catalyst is doubtless rhenium metal. Some methodical error such as coprecipitation probably caused the high values. [e] Analysis: Re, 84.1, 84.5%. [f] Analysis: Re, 82.9, 84.8%.

TABLE II

Conditions for the *ex situ* Reduction of Rhenium Heptoxide to Rhenium "Blacks" by Hydrogenation in the Presence of Trace Amounts (0.01 Formal Equivalent) of Extrinsic Catalytic Surface

Run No.	Trace Catalyst	Solvent	Avg. Temp. (°C.)	Avg. Pressure (atm.)	Time (hr.)	Comment
1	PtO_2	*p*-Dioxane	60	4	13	71% reduction[a]
12	PtO_2	Water	65	4	1	85% reduction[a]
7	Ru on C	*p*-Dioxane	60	4	12	100% reduction[b]
14	Ru on C	Water	65	4	5	100% reduction[b]
8	Re on C	*p*-Dioxane	76	4	8	46% reduction
9	Norit A[c]	*p*-Dioxane	76	4	10	37% reduction

[a] Precipitate had an olive drab cast. [b] Precipitate was an intense dull black. [c] Extrinsic surface provided by 58.5 mg. activated charcoal only/g. rhenium heptoxide.

thermocouple. The compound to be reduced (usually 0.1 or 0.2 mole), sometimes a solvent or diluent (usually absolute ethanol) to bring the total volume to 50 ml. and the catalyst (usually 1.0 g. rhenium/mole of substrate), all as indicated in the accompanying tables, were placed in the reactor. The catalyst was a rhenium "black," suspended in a diluent or the substrate in the *ex situ* reductions, or it was pure rhenium heptoxide in the *in situ* reductions. After adequate flushing to remove air, the reactor was then charged to a pressure of 2000 p.s.i.g. (136 atm.) or to 3000 p.s.i.g. (204 atm.). The hydrogenation was so managed as to obtain minimal conditions of reduction by operating at successively higher temperature increments until the reaction occurred readily, as outlined in more detail in Part I of this series.[1] In almost all cases more than one run of a kind was performed. Duplicability was good. After completion of the reaction as indicated by pressure drop, the reactor was cooled, vented and opened. The catalyst was filtered off for recovery or analysis and the solvent or diluent (if any) removed by distillation or extraction.

Analysis of reaction products was accomplished by fractional distillation, chemical extraction, spectrophotometry, titration, refractometry, and especially in the latter part of the problem by the exceptionally useful technique of gas chromatography.

Analysis of catalysts. (A) *Ultimate analysis.* After thorough washing and centrifugation from abs. ethanol, the catalyst was divided into portions in screw cap vials and dried in Abderhalden pistols *in vacuo* over phosphorous pentoxide or barium oxide with refluxing bromobenzene, nitrobenzene, or phenyl ether to constant weight. During the transferring and weighing operations they came in contact with a pure nitrogen atmosphere only. The weighed samples were dissolved in ammoniacal 30% hydrogen peroxide or with more refractory samples with concentrated nitric acid carefully added dropwise to the boiling mixture. The analyses were completed by precipitation and weighing the rhenium as tetraphenylarsonium perrhenate.[26]

B. *Oxidation state determination.* Large (*ca.* 1 g.) samples of the catalysts dried to constant weight were weighed into 125 ml. Erlenmeyer flasks and dissolved in a weighed (*ca.* 2-fold) excess of potassium dichromate, 1.0 ml. sulfuric acid and 10–25 ml. distilled water. After completion of the oxidation, the unused dichromate was reduced with excess potassium iodide. The liberated iodine was titrated with 0.1*N* sodium thiosulfate to the starch end-point. These data together with a knowledge of the rhenium content of the sample enabled a determination of the oxidation state of the rhenium in the catalyst.

Discussion of Results. The authors have chosen the term *ex situ* to describe the reactions carried out using a catalyst which had been previously prepared by hydrogenation of rhenium heptoxide *out of the site* of the substrate subsequently to be reduced by the catalyst; the term *in situ* has been chosen to describe those reactions in which

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TABLE III

A COMPARISON OF THE CATALYTIC ACTIVITY OF RHENIUM "BLACKS" DERIVED FROM RHENIUM HEPTOXIDE BY *ex situ* REDUCTION WITHOUT EXTRINSIC CATALYSIS

No.	Substrate	Solvent for Catalyst Preparation	Amt. Cat. g./mole	Solvent for Reduction	Avg.[a] Temp. (°C.)	Avg.[a] Pressure (atm.)	Time[a] (hr.)	Yield(s),[b] %	Product(s)
1	Nitrobenzene	*p*-Dioxane	2.5	Ethanol	110	150	4	100	Aniline
2	Nitrobenzene	Acetic acid	2.1	Ethanol	100	160	12	90	Aniline
3	Nitrobenzene	Ethanol	2.5	Ethanol	100	143	3	100	Aniline
4	Nitrobenzene	Water	1.0	Ethanol	108	243	12	34	Aniline
5	Styrene	*p*-Dioxane	1.0	Ethanol	108	156	3.5	100	Ethylbenzene
6	Styrene	Acetic acid	3.0	Ethanol	170	207	2.5	24	Ethylbenzene
7	Styrene	Ethanol	2.0	Ethanol	130	170	22	0	100% polymer
8	Acetophenone	*p*-Dioxane	2.9	Ethanol	60	143	18	78	Methylphenylcarbinol
9	Acetophenone	Acetic acid	2.5	Ethanol	67	143	4.5	38	Methylphenylcarbinol
10	Acetophenone	Ethanol	2.6	Ethanol	155	184	14	47	Methylphenylcarbinol
11	Acetophenone	Water	1.0	Ethanol	135	242	9.5	50	Methylphenylcarbinol
12	Cyclohexanone	Acetic acid	2.5	None	64	143	12	84	Cyclohexanol
13	Acetic acid	*p*-Dioxane	1.0	None	147	355	9	40	Ethanol, 41% ethyl acetate
14	Acetic acid	Acetic acid	0.2	None	160	129	60	68	Ethanol, 41% ethyl acetate
15	Acetic acid	Ethanol	1.1	None	146	258	15	38	Ethanol, 41% ethyl acetate
16	Acetic acid	Water	1.1	None	175	275	2.5	27	Ethanol, 41% ethyl acetate
17	Maleic acid	*p*-Dioxane	2.6	*p*-Dioxane	148	177	2.5	100	Succinic acid
18	Maleic acid	Acetic acid	2.5	*p*-Dioxane	158	163	12	93	Succinic acid
19	Maleic acid	Ethanol	1.1	Water	151	254	4	100	Succinic acid
20	Maleic acid	Water	1.0	Water	200	194	8	0	Succinic acid
21	Succinic acid	Water	1.1	Water	205	272	12	39	Tetrahydropyran
								35	1,4-Butanediol
								6	*n*-Butyl alcohol
22	Crotonaldehyde	*p*-Dioxane	1.0	None	145	152	1.25	94	Crotyl alcohol
								3	Butyraldehyde
								3	Crotonaldehyde
23	Cinnamic acid	Acetic acid	2.5	*p*-Dioxane	160	176	3	55	Hydrocinnamic acid
								39	Hydrocinnamyl hydrocinnamate
								6	Hydrocinnamyl alcohol
24	Isobutyl isobutyrate	Acetic acid	1.0	None	165	176	5	59	Isobutyl alcohol
								41	Isobutyl isobutyrate

[a] Figures in these columns refer to the average temperature (usually quite constant) and average total system pressure during the time of hydrogenation. [b] The yield's column shows only reduced products. Unless otherwise specified the remainder of recovered material was unreduced substrate. The percentage figure given is based on 100% recovery of all products of reaction. Because of mechanical loss etc. the recovery was always slightly less than this. These same considerations apply to all other Tables given in this paper.

the rhenium heptoxide was added directly to the substrate and hydrogenated to the "black" *in the presence* of the substrate subsequently and/or simultaneously being reduced through the agency of the catalyst.

Preparation of catalysts. The ease of *ex situ* reductions of rhenium heptoxide to rhenium "blacks" was found to vary markedly with the solvent or suspending medium (see Table I). Thus conditions for reaction were rather mild in *p*-dioxane or water solution, less so in acetic acid, and relatively drastic in ethanol. Moreover, their physical appearance as well as catalytic activity was found to be greatly different. The material obtained in acetic acid was largely colloidal whereas that from *p*-dioxane was a dull black powder and that from ethanol or water lustrous, metallic flakes. In the absence of any extrinsic catalytic surface, the heptoxide is at first very slowly reduced on the walls of the containing vessel during the relatively long induction period, followed by a relatively rapid reduction of the remaining heptoxide, predominantly on the surface of the material already formed.

As evidence for this hypothesis, it was found that traces (0.01 formal equivalents) of extrinsic catalytic surfaces such as platinum oxide, activated carbon, or previously prepared rhenium black enormously increased the ease of reduction of rhenium heptoxide (Table II). These traces of added material were present in amounts too small to be catalytically significant in the hydrogenation reactions subsequently observed with the rhenium blacks formed in their presence. The ease of reduction of the heptoxide did not seem to depend greatly on the nature of the added surface among those examined, although there were some differences. The hydrogenation promotion activity did so depend, as will be evident below. Alcohol as a solvent was found to demand more drastic conditions for reduction just as when extrinsic surface was absent. On the other hand while the yields of

TABLE IV

COMPARISON OF THE CATALYTIC ACTIVITY OF RHENIUM "BLACKS" DERIVED FROM RHENIUM HEPTOXIDE BY *ex situ* REDUCTION WITH VARIOUS EXTRINSIC CATALYSTS

No.	Substrate	Amt. Cat. g./mole	Trace[a] Catalyst	Solvent for Reduction	Avg. Temp. (°C.)	Avg. Pressure (atm.)[b]	Time (hr.)	% Yields, Product
1	Nitrobenzene	1.0	PtO_2	Ethanol	215	285	4	64% Aniline
2	Styrene	1.1	PtO_2	Ethanol	110	238	2	100% Ethylbenzene
3	Acetophenone	0.8	PtO_2	Ethanol	80	224	3	70% Methylphenylcarbinol, 30% ethylbenzene
4	Acetophenone	1.3	Ru on C	Ethanol	93	251	9	91% Methylphenylcarbinol, 9% ethylbenzene
5	Acetophenone	0.5	Norit A	Ethanol	155	258	3	50% Methylphenylcarbinol, 8% ethylbenzene
6	Acetophenone	1.1	Re	Ethanol	150	256	3	100% Methylphenylcarbinol
7	Acetic acid	1.1	PtO_2	None	200	286	7	43% Ethanol, 30% ethyl acetate
8	Maleic acid	1.0	PtO_2	Water	180	290	3	52% Succinic acid

[a] The catalyst was obtained in each case by reduction of rhenium heptoxide at low temperature and pressure in *p*-dioxane solution in the presence of traces (0.01 mole equivalent) of extrinsic catalysts. [b] Total pressure under the conditions of hydrogenation at the temperature shown.

insoluble rhenium black were substantially quantitative in every case under the high temperature-high pressure conditions, the yields in the relatively mild extrinsically catalyzed procedures were not always quantitative, and the product then had the greenish yellow cast of unreduced heptoxide.

Catalytic activity of rhenium heptoxide reduced ex situ in the absence of extrinsic catalytic surface. In Table III some data are presented comparing the activity of the rhenium blacks obtained in the four solvents, *p*-dioxane, acetic acid, ethanol, and water, in the hydrogenation of several representative types of compounds. While the pattern of behavior is different for the catalysts prepared in each of the different solvents, that obtained from water is least effective. The differences are relatively small against nitrobenzene and acetic acid; however, against styrene that obtained from *p*-dioxane is markedly superior; against acetophenone the use of either *p*-dioxane or acetic acid is decidedly better than ethanol or water, and against maleic acid water is much inferior to the other solvents as a vehicle for the preparation of the catalyst.

As far as general hydrogenation catalytic activity is concerned these substances are relatively unexceptional in their behavior toward the compounds reduced by most known catalysts: nitrobenzene, styrene, acetophenone, olefinic bond of maleic acid. However, it will be noticed that the carbonyl function was more easily reduced than the olefinic—the reverse of the most commonly observed catalytic behavior. Advantage of this fact was realized in the noteworthy reduction of crotonaldehyde to crotyl alcohol in high yield. Corresponding attempts with cinnamaldehyde resulted only in resinification—perhaps because of traces of unreduced rhenium heptoxide which yields the strong perrhenic acid in the presence of moisture.

Furthermore, attention should be particularly called toward the uniquely high activity displayed in promoting the reduction of the carboxyl function (acetic acid, succinic acid, cinnamic acid). Rhenium heptoxide *in situ* (see below) displays this activity to a much higher degree. The analytical data suggest that the active catalyst is rhenium metal when prepared in *p*-dioxane or ethanol solution and rhenium dioxide when prepared in water or acetic acid; however, in the last two cases hydrated forms of still lower oxides may well be involved, as oxidation state determinations made on rhenium heptoxide reduced in acetic acid in the presence of excess water (see below) indicates hydrated rhenium monoxide to be the active form of the catalyst.

In the presence of extrinsic surfaces the rhenium blacks, which were obtained in high yields, had the same general but slightly lower degree of activity as those obtained under more drastic conditions in the absence of extrinsic catalytic surface, with the exception of nitrobenzene substrate. This exception is probably attributable to the presence of traces of unreduced rhenium heptoxide, which appears to have a very adverse effect on the reduction of this function as will later appear. The two rhenium black preparations obtained in low yield (Runs 8 and 9, Table II) were anomalous in that they were much less effective catalysts (*cf.* Nos. 5, 6, Table IV), probably because they were different in composition from the others. Taken as a whole the evidence of the catalysts prepared in the presence of extrinsic surfaces is of interest principally because of the light it may shed on the mechanism of reduction of rhenium heptoxide solutions to insoluble rhenium blacks. In a practical sense they offer no advantage over the catalysts formed in the absence of extrinsic surfaces.

Hydrogenations catalyzed by rhenium heptoxide reduced in situ. A small but representative fraction of the data obtained by adding pure, dry rhenium

TABLE V

HYDROGENATIONS WITH RHENIUM HEPTOXIDE REDUCED *in situ* AS CATALYST

No.	Substrate	Solvent	Avg. Temp. (°C.)	Avg. Pressure (atm.)[g]	Time (hr.)	Yields, %, Product(s)
1	Benzene[a]	None	330	232	13	49% Benzene, 11% cyclohexane, gaseous hydrocarbons
2	Cyclohexene[a]	None	100	156	6	98% Cyclohexane
3	1-Hexene[b]	None	100	150	2.5	100% Hexane
4	Styrene[b]	Ethanol	109	165	4	86% Ethylbenzene, 14% polymer
5	Nitrobenzene[a]	Ethanol	250	204	3	0% Aniline
6	Nitrobenzene[a]	None	165	143	3	100% Aniline
7	Cyclohexanone[b]	Ethanol	154	270	3	100% Cyclohexanol
8	Acetophenone[a]	Ethanol	115	160	18	100% Condensation products
9	Formic acid[a]	None	240	238	12	100 mg. "Polymethylene," ca. 98% water, much methane, 1% carbon dioxide
10	Acetic acid[a]	None	150	163	10	77% Ethanol, 23% ethyl acetate
11	Acetic acid[b]	Water	150	168	10	100% Ethanol
12	Trifluoroacetic acid[b]	Water (20 ml.)	207	300	18.5	100% Trifluoroethanol
13	Dichloroacetic acid[b]	Water (20 ml.)	220	315	11.5	0% Reduction
14	Trichloroacetic acid[b]	Water (20 ml.)	172	298	27	0% Reduction
15	Propionic acid[a]	None	165	252	1.5	92% *n*-Propyl alcohol, 8% *n*-propyl propionate
16	Formic acid + propionic acid[a]	None	250	224	2.3	67% *n*-Propyl alcohol, 29% *n*-propyl formate, 4% *n*-propyl propionate
17	Butyric acid[a]	None	163	153	4.5	70% *n*-Butyl alcohol, 30% *n*-butyl butyrate
18	Butyric acid[b]	Water (3 ml.)	150	178	11	89% *n*-Butyl alcohol, 11% *n*-butyl butyrate
19	Heptafluorobutyric acid[b]	Water (20 ml.)	190	302	17	70% Heptafluorobutanol, 29% heptafluorobutyl heptafluorobutyrate
20	Isobutyric acid[a]	None	165	156	4	75% Isobutyl alcohol, 28% isobutyl isobutyrate
21	Valeric acid[a]	None	160	173	10	55% *n*-Amyl alcohol, 43% *n*-amyl valerate
22	Pivalic acid[a]	None	264	248	5	0% Reduction
23	Caproic acid[a]	None	174	170	3.2	61% *n*-Hexyl alcohol, 39% *n*-hexyl caproate
24	Caproic acid[b]	Water (4.5 ml.)	200	188	2	93% *n*-Hexyl alcohol, 7% *n*-hexyl caproate
25	Caprylic acid[a]	None	163	163	2.5	52% *n*-Octyl alcohol, 48% *n*-octyl caprylate
26	Caprylic acid[b]	Water (50 ml.) and *p*-dioxane	163	193	14	100% *n*-Octyl alcohol
27	Capric acid[a]	None	164	169	2.5	70% *n*-Decyl alcohol, 30% *n*-decyl caproate
28	Capric acid[b]	Water (25 ml.) and *p*-dioxane	137	173	3.5	100% *n*-Decyl alcohol
29	Lauric acid[a]	None	145	177	8	42% *n*-Dodecyl alcohol, 58% *n*-dodecyl laurate
30	Lauric acid[b]	Water (10 ml.) and *p*-dioxane	160	186	10	100% *n*-Dodecyl alcohol
31	Stearic acid[a]	None	167	268	5	36% *n*-Octadecyl alcohol, 54% *n*-octadecyl stearate
32	Stearic acid[b]	Water (10 ml.) and *p*-dioxane	265	245	23.5	43% *n*-Octadecyl alcohol, 29% stearic acid, 28% unknown
33	Benzoic acid[a]	Benzene	254	190	15	91% Toluene
34	Phenylacetic acid[a]	None	149	160	14	78% β-Phenylethyl alcohol, 22% β-phenylethyl phenylacetate
35	Lactic acid[a]	None	150	258	8	84% Propylene glycol, 16% lactic acid and lactide
36	Crotonic acid[a]	None	163	150	12	30% *n*-Butyl alcohol, 70% *n*-butyl butyrate
37	Levulinic acid[a]	None	106	150	18	71% γ-Valerolactone, 29% polymeric esters
38	Glycine[a]	*p*-Dioxane	220	326	14	72% Glycine, 6% ethanol, 11% β-aminoethyl glycinate
39	β-Alanine[a]	*p*-Dioxane	250	300	8	24% β-Alanine, 35% *n*-propyl alcohol, 41% *n*-propyl 3-aminopropionate
40	β-Alanine[b]	Water (50 ml.)	250	210	32	92% *n*-Propyl alcohol, 4% β-alanine, 4% unknown
41	Maleic acid[a]	None	196	286	12	91% Succinic acid, 9% 1,4-butanediol
42	Succinic acid[a]	*p*-Dioxane	205	184	30	61% Butyrolactone, 33% 1,4-butanediol, 6% polyesters
43	Succinic acid[a]	None	210	245	4	94% 1,4-Butanediol, 6% *n*-butyl alcohol
44	Succinic acid[a]	Water	210	258	6.5	13% Tetrahydrofuran, 59% 1,4-butanediol, 3% polyesters
45	Glutaric acid[a]	*p*-Dioxane	210	184	5	82% 1,5-Pentanediol, 18% polyesters
46	Glutaric acid[b]	Water (50 ml.)	250	179	50	100% 1,5-Pentanediol

TABLE V (*Continued*)

No.	Substrate	Solvent	Avg. Temp. (°C.)	Avg. Pressure (atm.)[g]	Time (hr.)	Yields, %, Product(s)
47	Ethyl acetate[b]	None	148	191	11	100% Ethanol
48	Ethyl benzoate[b]	Cyclohexane	250	290	48	89% Benzyl alcohol, 11% ethyl benzoate[e]
49	Isobutyl formate[a]	None	165	167	2	35% Methanol, 35% isobutyl alcohol
50	Isobutyl isobutyrate[a]	None	151	340	3	57% Isobutyl alcohol
51	Azobenzene[b]	Cyclohexane	125	249	24	92% Aniline
52	Hydrazobenzene[b]	Cyclohexane	185	280	42	97% Aniline
53	Acetamide[b]	Cyclohexane	217	312	6	39% Ethylamine[f]
54	Acetanilide[b]	Cyclohexane	170	280	52	66% *N*-Ethylaniline, 34% aniline[e]
55	*N*-Ethylacetanilide[b]	Ethanol	245	352	22	95% *N*,*N*-Diethylaniline, 5% unidentified

[a] Amount of catalyst used: 1.0 g. Re/mole of substrate. [b] Amount of catalyst used: 1.0 g. Re/50 g. substrate. In later work it was deemed more desirable in comparing compounds of greatly differing molecular weights to use weight rather than molar ratios. [c] A small button of translucent white waxy resin was obtained, softening at 106° and melting at 121–122° with slow (1/2 hr.) heating. (*cf.* 111° melting of high pressure process polyethylene; 132°, Ziegler process polyethylene). *Anal.* Found: C, 85.4, 85.60%; H, 14.50, 14.53%. Calcd. for $C_{100}H_{202}$: C, 85.51%; H, 14.49%. Its properties and analysis suggest it to be a high molecular weight paraffinic resin. If this substance were a straightchain hydrocarbon its high melting point as well as its analysis would suggest a chain length of >70 carbon atoms (heptacontane melts at 105°); however, the molecular weight (Rast) indicates 30–33 carbon atoms. There seems reason to question the validity of the molecular weight determination in this case. [d] This run consisted of the hydrogenation of an equimolar mixture of the two acids. The yield data are adjusted to 100% excluding the methane and water formed by hydrogenation of most of the formic acid. No "polymethylene" was formed in this run. [e] Yields given are based on residue obtained after evaporating off the ethanol and cyclohexane. [f] A leak which developed during the hydrogenation resulted in the loss of considerable of the volatile amine while the reaction was in progress. [g] Total pressure in the system at the temperature shown.

heptoxide directly to a substrate followed by hydrogenation is presented in Table V. This is the most significant group of findings reported in this paper not only because of the simplicity of the procedures but also because of some of the remarkable transformations which can be accomplished.

In every case the rhenium can be recovered from the reactor as an insoluble black following hydrogenation. Analysis showed a rhenium content of 83.82, 83.75, 82.80% for the rhenium black obtained in the hydrogenation of acetic acid without solvent. No oxidation state determinations were made. The rhenium black resulting when carrying out the hydrogenation of acetic acid in water solution gave values of 88.17, 89.20, 90.54% rhenium in successive examples with corresponding values of 5.43, 5.19, and 5.31 equivalents of dichromate required for oxidation to +7 state. This suggests that the catalyst may be a hydrated rhenium monoxide.

Benzene and olefins are reduced by rhenium heptoxide *in situ* more difficultly than with many common catalysts. Nitrobenzene is much more difficultly reduced by rhenium heptoxide *in situ* than by the catalyst obtained *ex situ*. The peculiar, adverse effect of ethanol solvent in this reaction is common to other rhenium oxide catalysts which have been studied. Acetophenone is converted completely to complex condensation products, doubtless because of the highly acidic character of rhenium heptoxide.

Most outstanding among the reactions which rhenium heptoxide derived catalysts promote is the extraordinarily facile reduction of carboxylic acids to alcohols. These transformations occur at 150–170° for monocarboxylic acids, 200–250° for dicarboxylic acids, under 135–270 atm. total operating pressure in a few hr. Virtually no unreduced acid survives the reaction.

The effect of carrying out the hydrogenations of acids in the presence of solvent water as contrasted to reactions run without added water is particularly noteworthy. (*Cf.* Table V, Nos. 10, 11; 17, 18; 23, 24; 25, 26; 27, 28; 29, 30; 31, 32; 39, 40; 45, 46.) While the hydrogenations run on the anhydrous acids always resulted in some by-product ester formation, those run in water solvent gave markedly reduced ester formation, or in most cases no ester by-product at all. The mechanism of this effect is not definitely understood although a number of experiments were carried out testing various hypotheses.

The conditions for carrying out these hydrogenations are in general 100–250° lower than required for the same or closely similar transformations previously recorded, with the exception of the use of ruthenium dioxide.[19] In the latter case the conditions of time, temperature, and yields for a much more limited set of reported examples are comparable, but the pressures required appear to be much greater.

The rhenium heptoxide catalyzed hydrogenation of carboxylic acids is apparently general for the normal homologous series beginning with acetic acid and also for not too highly branched isomers. It is also successful with dicarboxylic acids.

The reduction occurs with various substituted acids: phenylacetic acid is reduced to β-phenylethyl alcohol without affecting the aromatic ring; lactic acid yields propylene glycol; crotonic acid yields *n*-butyl alcohol; levulinic yields predominantly γ-valerolactone. The amino acids, glycine, and

TABLE VI

COMPARISON OF THE CATALYTIC ACTIVITY OF PLATINUM DIOXIDE, RANEY NICKEL, COPPER–CHROMIUM OXIDE, AND RHENIUM HEPTOXIDE IN THE HYDROGENATION OF FIVE REPRESENTATIVE SUBSTRATES

Substrate	Catalyst	Amt. Cat. g./mole	Avg. Temp. (°C.)	Avg. Pressure (atm.)[a]	Time (hr.)	% Yields, Product
Nitrobenzene	PtO_2	1.0	25	4[b]	0.25	100% Aniline
	Ni	3.0	25	4[b]	0.25	100% Aniline
	$CuO{\cdot}CuCr_2O_4$	8.0	205	163	1.5	98% Aniline
	Re_2O_7[e]	2.1	100	159	12	90% Aniline
Styrene	PtO_2	1.0	25	4[b]	0.25	100% Ethylbenzene
	Ni	3.0	30	4[b]	1.5	100% Ethylbenzene
	$CuO{\cdot}CuCr_2O_4$	8.0	122	146	0.33	82% Ethylbenzene
	Re_2O_7[e]	1.0	108	156	3.5	100% Ethylbenzene
Cyclohexanone	PtO_2	1.0	25	4[b]	5	91% Cyclohexanol
	Ni	3.0	60	4[b]	3	92% Cyclohexanol
	$CuO{\cdot}CuCr_2O_4$	8.0	115	150	0.25	94% Cyclohexanol
	Re_2O_7[e]	2.5	64	143	12	84% Cyclohexanol
Isobutyl isobutyrate	PtO_2	1.0	320	252	5	5% Isobutyl alcohol
	Ni	2.5	315	368[c]	4.5	0% Isobutyl alcohol
	$CuO{\cdot}CuCr_2O_4$	21.0	180	272[c]	2.5	100% Isobutyl alcohol
	Re_2O_7[f]	1.0	151	340[d]	3	57% Isobutyl alcohol
Acetic acid	PtO_2	1.0	300	258	12	0% Ethanol, 7% ethyl acetate
	Ni	3.0		Catalyst dissolves—no hydrogenation		
	$CuO{\cdot}CuCr_2O_4$	8.0	250	306[c]	21	0% Ethanol, 20% ethyl acetate
	Re_2O_7[f]	2.0	150	168	10	100% Ethanol

[a] Total pressure during hydrogenation at the temperature given. Initial pressure of hydrogen at room temperature was 136 atm. unless otherwise specified. [b] Initial hydrogen pressure was 4 atm. at room temperature. [c] Initial hydrogen pressure was 204 atm. at room temperature. [d] Initial hydrogen pressure was 272 atm. at room temperature. [e] Reduced *ex situ*. [f] *In situ.*

β-alanine, are anomalous in that the alcohol obtained is deaminated. Di- and trichloroacetic acids were not successfully reduced, but both trifluoroacetic acid and heptafluorobutyric acids gave the corresponding alcohols in excellent yields.

Formic acid is exceptional in that the temperature required for reduction is nearly 100° above that for other monocarboxylic acids and the principal reduction product is methane accompanied by small amounts of "polymethylene," a high molecular weight, paraffinic resin. The addition of small amounts of (5 mole %) di-*tert*-butyl peroxide to the formic acid did not alter the amount of "polymethylene" formed, but that which was obtained had a much lower molecular weight.

The highly branched trimethylacetic (pivalic) acid could not be reduced to any recognizable product even at 264°. Some uncharacterized resinous material resulted. This is not unexpected, as there is no way for the trimethylacetic acid molecule to be absorbed flat on the catalytic surface.

The optimum temperature for alcohol formation from acetic acid was 150°; at 240° it was slowly converted to ethane.

A comparison of the catalytic activity of platinum dioxide, Raney nickel, copper–chromium oxide and rhenium heptoxide (Table VI). These data represent actual experimental comparisons made in our laboratories in order to minimize the effects of apparatus and procedure. Rhenium heptoxide reduced *ex situ* is less effective in catalyzing reduction of nitrobenzene, styrene, or cyclohexane than either platinum dioxide or Raney nickel, more effective than copper–chromium oxide. Copper–chromium oxide is the best in the reduction of isobutyl isobutyrate with rhenium heptoxide next; platinum dioxide and Raney nickel fail completely. Against acetic acid rhenium heptoxide *in situ* is the only one which is effective.

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