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).

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

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ent of the order or mode of addition of salt and alkali metal or of the relative proportions of reactants and solvent; however, the catalyst activity did appear to depend significantly on the chemical system used. The catalyst prepared by reduction with lithium in ethylamine was somewhat superior, in general, to that obtained with lithium in liquid ammonia or to the catalyst obtained by reduction with sodium in liquid ammonia, with some exceptions.

The use of potassium as a reducing agent was not successful. The traces of solid reduction product initially formed catalyzed the reaction of potassium with the solvent so strongly that essentially nothing but potassium amide could be obtained.

Sodium metal proved to be insufficiently soluble in ethylamine to function effectively in that solvent.

Only a poor yield of catalyst could be obtained from lithium in ethylenediamine.

Curiously, the reduction of ammonium perrhenate, which was accomplished so successfully by sodium in liquid ammonia, failed entirely with solutions of potassium perrhenate in liquid ammonia. Relatively very large proportions of sodium were rapidly converted to sodium amide with evolution of hydrogen, but no appreciable amount of perrhenate was reduced. A possible explanation of this phenomenon is suggested by the following reactions.

$$KReO_4 + Na^0 \rightleftharpoons K^0 + NaReO_4 \qquad (1)$$

$$K^0 + NH_3 \longrightarrow KNH_2 + 0.5H_2 \qquad (2)$$

$$KNH_2 + Na^0 \rightleftharpoons K^0 + NaNH_2 \qquad (3)$$

In spite of the unfavorable equilibrium of equation 1, the essential irreversibility of 2 and the favorable equilibrium of 3, caused by the markedly lower solubility of sodium amide than potassium amide, drive the reaction on to completion.

Although rhenium(VII) oxide was reduced as readily as ammonium perrhenate, the extreme hygroscopicity of the former with consequent difficulties in handling made use of the latter substance preferable.

Approximate determinations of the solubilities of potassium perrhenate, ammonium perrhenate, and rhenium heptoxide in liquid ammonia were made.

Experimental

Catalyst Preparation. A. Apparatus.—Both the solubility determinations and the alkali metal reductions were performed in a scrupulously dried Minilab[16] reactor system (100 ml. and 200 ml.) fitted with a sealed ground-glass sleeve stirrer, Dry Ice condenser, and drying tube. One of the two remaining outlets was connected directly to the ammonia cylinder (or sealed when ethylamine was used) and the other was used to introduce the reactants. Back flushing with dry nitrogen supplied through the drying tube connection protected the system from moisture and oxygen whenever the system was open to the atmosphere momentarily. A fritted glass filter disk sealed in the bottom of the reaction flask was connected through a stopcock to a Dry Ice-cooled, graduated receiver and thence to suction. To avoid problems in the operation of the stopcock, it was mounted in an upturned glass loop above the level of the liquid in the reactor.

B. Solubility Determinations.—Excess rhenium compound was introduced into the dried, nitrogen-flushed reactor. Then, liquid ammonia was condensed into the system and stirred until no more of the rhenium compound would dissolved. The solution was then filtered into the cooled, graduated receiver, allowed to evaporate, and the residue weighed.

TABLE I

A COMPARISON OF THE CATALYTIC HYDROGENATION ACTIVITY OF $ReO \cdot 2H_2O$ CATALYST DERIVED BY SODIUM–AMMONIA (TYPE A), LITHIUM–AMMONIA (TYPE B), AND LITHIUM–ETHYLAMINE (TYPE C) REDUCTIONS[a]

No.	Substrate[b]	Catalyst type	Av. temp., °C.	Time, hr.	Product	Yield, %
1	Butanone	A	128	3	2-Butanol	100
	Butanone	B	111	4	2-Butanol	100
	Butanone	C	100	2.5	2-Butanol	100
2	Cyclohexanone	A	165	4	Cyclohexanol	100
	Cyclohexanone	B	120	15	Cyclohexanol	100
	Cyclohexanone	C	119	2.5	Cyclohexanol	100
3	1-Hexene	A	122	4	Hexane	100
	1-Hexene	B	104	0.5	Hexane	100
	1-Hexene	C	119	2.5	Hexane	100
4	Cyclohexene	A	120	3	Cyclohexane	100
	Cyclohexene	B	99	22	Cyclohexane	100
	Cyclohexene	C	105	16	Cyclohexane	100
5	Styrene (ethanol)	A	108	3	Ethylbenzene	85
	Styrene (ethanol)	B	70	12	Ethylbenzene	56
	Styrene (ethanol)	C	30	11	Ethylbenzene	64
6	Benzene	A	202	10	Cyclohexane	67
	Benzene	B	206	12	Cyclohexane	34
	Benzene	C	225	3	Cyclohexane	50
7	Nitrobenzene (ethanol)	A	160	6	Aniline	88
	Nitrobenzene (ethanol)	B	113	18	Aniline	75
	Nitrobenzene (ethanol)	C	106	7	Aniline	91
8	Acetic acid (water)	A	178	7	Ethanol	100
	Acetic acid (water)	C	145	4.5	Ethanol	100

[a] In each run 0.10 or 0.20 g. of catalyst and 0.10 or 0.20 mole of substrate were used, respectively. [b] Reaction solvent, if any, is indicated in parentheses.

Successive determinations gave the solubility of potassium perrhenate in liquid ammonia at −33° as 7.4 g./100 ml. of solution. Ammonium perrhenate was so soluble that the solution became so viscous as to make filtration very difficult and only a minimum value could be obtained. The solubility of ammonium perrhenate in liquid ammonia is >83 g./100 ml. of solution. The solubility of rhenium(VII) oxide in liquid ammonia presented even greater problems. It is apparently as soluble as ammonium perrhenate, perhaps more so.

C. Rhenium(II) Oxide.—Fifty to seventy-five milliliters of ammonia or ethylamine was introduced into the flask, and a weighed amount (1–2 g.) of ammonium perrhenate was added with stirring. After the salt was dissolved 15 to 30 g.-atoms of sodium or lithium was added in small chunks as rapidly as possible. The colorless solution quickly acquired the blue-black metallic sheen typical of solutions of metals in ammonia. The mixture was stirred until the blue-black color disappeared (usually 15 min. to 2 hr.). The ammonia or ethylamine was either removed by filtration or allowed to evaporate being simultaneously replaced by ethanol. The contents of the flask were then transferred to a fritted glass thimble in a Soxhlet apparatus and extracted with dilute hydrochloric acid for 24 hr. followed by extraction with ethanol for an equal time. During the acid extraction the solution in the pot acquired a brown color. This brown solution would decolorize permanganate. Addition of ammonium hydroxide precipitated a black powder leaving a colorless supernatant solution no longer decolorizing permanganate. This precipitate appeared to have the same composition and properties as that remaining in the Soxhlet thimble. Following extraction the rhenium(II) oxide product remaining in the thimble was stored suspended in ethanol. The recovery of rhenium in this form amounted to 75–85% of that in the starting perrhenate.

D. Analysis of Catalyst. Rhenium.—Samples were prepared for analysis by centrifugation of aliquots of the ethanol suspensions, decantation, and vacuum drying of the residues which were weighed under nitrogen atmosphere, and the analyses completed as described previously,[17] or by a more recent photometric procedure[18] based on the absorption at 281 mμ of the hexachlororhenate ion. The latter method worked very well on pure perrhenate standards, but the small excess of oxidant required in dissolving the catalyst samples interfered with the reduction of perrhenate to hexachlororhenate by chromous chloride; moreover, the absorbancy of the resulting solutions was rather time dependent.

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[16] A small scale all-glass apparatus made by the Ace Glass Co., Vineland, N. J.

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

[18] V. W. Meloche and R. L. Martin, *Anal. Chem.*, **28**, 1671 (1956).

TABLE II

HYDROGENATIONS CATALYZED BY $ReO \cdot 2H_2O$[a] DERIVED BY SODIUM IN LIQUID AMMONIA REDUCTION OF AMMONIUM PERRHENATE

No.	Substrate	Av. temp., °C	Time, hr.	Product(s)	Yield, %
1	Acetone	78	10	2-Propanol	100
2	Butanone	116	6	2-Butanol	100
3	3-Methyl-2-butanone	198	7	3-Methyl-2-butanol	100
4	2,3-Butanedione	93	7.5	2,3-Butanediol, four unidentified products	50
5	2-Pentanone	136	11	2-Pentanol	100
6	3-Pentanone	160	6	3-Pentanol	100
7	4-Methyl-2-pentanone	180	5	4-Methyl-2-pentanol	100
8	2,4-Pentanedione	132	12	2,4-Pentanediol, six unidentified products	50
9	Cyclopentanone	167	6	Cyclopentanol	100
10	2-Hexanone	135	11.5	2-Hexanol	100
11	2,5-Hexanedione	121	10.5	2,5-Hexanediol	95
12	Cyclohexanone	172	10	Cyclohexanol	100
13	2-Heptanone	172	3.5	2-Heptanol	96
14	3-Heptanone	152	5	3-Heptanol	100
15	4-Heptanone	186	2	4-Heptanol	98
16	Cycloheptanone	175	8.5	Cycloheptanol	100
17	2-Octanone	130	6	2-Octanol	86
18	2-Nonanone	178	6	2-Nonanol	100
19	Acetophenone	125	9	Methylphenylcarbinol	67
20	2-Hexene	151	3	Hexane	100
21	5-Hexen-2-one	119	6	2-Hexanone	71
				2-Hexanol	29

[a] In each run 0.20 mole of substrate was hydrogenated using 0.10 g. of catalyst.

TABLE III

HYDROGENATIONS CATALYZED BY LITHIUM–LIQUID AMMONIA DERIVED $ReO \cdot 2H_2O$[a]

No.	Substrate[b]	Av. temp., °C.	Time, hr.	Product(s)	Yield, %
1	Acetophenone	158	5	Methylphenylcarbinol	64
				Ethylbenzene	36
2	2,4,4-Trimethyl-1-pentene	200	0.5	2,4,4-Trimethylpentane	100
3	*p*-Chlorostyrene (ethanol)	90	13	*p*-Chloroethylbenzene	52
				Polymer	48
4	5-Hexen-2-one (ethanol)	81	6	2-Hexanone	72
				2-Hexanol	28
5	2-Allylcyclohexanone (ethanol)	123	14	2-Propylcyclohexanone	88
				2-Propylcyclohexanol	4

[a] In each run either 0.10 or 0.20 mole of substrate was hydrogenated with a catalyst–substrate ratio of 1.0 g./mole substrate. [b] Reaction solvent, if any, is indicated in parentheses.

Anal. Calcd. for $ReO \cdot 2H_2O$: Re, 78.3. Found: 78.4, 79.1. Determinations on lithium or sodium (flame photometry) and nitrogen (Kjeldahl) were completely negative. The rhenium content was the same for all three types of catalyst (A, B, or C).

Oxidation State.—The average of five determinations by the method reported earlier[17] gave a value of 5.00 for the change in oxidation number in oxidizing the rhenium catalyst to perrhenate [Re(II) → Re(VII)].

Hydrogenation Procedure.—Four different hydrogenation apparatus were employed: (a) an Aminco 500-ml. rocking reactor, with glass liner, rocking at 36 cycles/min.; (b) a 500-ml. Parr reactor, with glass liner, rocking at 36 cycles/min.; (c) a 300-ml. "Magnedash" reactor, without liner, agitated by a variable magnetically operated dasher usually operated at 50 cycles/min.; and (d) a 280-ml. "Pendaclave" reactor, with glass liner, shaking at 80 cycles/min. So far as could be determined, the particular reactor chosen for a given hydrogenation made no significant difference in the conditions necessary for the reduction of a given substrate. Operating temperatures and pressures were simultaneously recorded on a Leeds & Northrup X_1-X_2 recorder *via* iron-constantan thermocouple and Baldwin strain gage transducers, respectively.

The operating procedure was that reported earlier,[17] designed to give minimal temperatures consistent with reasonable rates of hydrogenation. In every case an initial operating pressure of 200 atm. of hydrogen was arbitrarily chosen. Each batch of catalyst prepared by a given procedure was checked for its ability to catalyze the hydrogenation of butanone.

Analysis of Products.—In those cases where only one reduction product was obtained and no solvent was used, analyses were determined by refractive indexes. In all other cases analyses were performed by gas chromatography. For each chemical system experiments were conducted to determine optimum column substrates and operating temperatures. Excellent analytical separations were achieved in each case.

Discussion

A minor, but representative, selection of the more than 160 hydrogenations carried out with $ReO \cdot 2H_2O$ catalyst are presented in the accompanying tables.

Table I gives a comparison of the catalytic activities of the oxide prepared in three different chemical systems against eight organic substrates. These data are not repeated in other tables. It will be noted that while the differences in activities of the three different catalyse preparations are not great in most cases, there is a general trend indicating the type C catalyst is more active than types A and B.

Table II illustrates the conditions under which a variety of ketones undergo hydrogenation. Attention is called particularly to the selectivity of hydrogenation of acetophenone (**19**), showing the unreduced benzene ring and the relative stability of the benzylic hydroxyl to hydrogenolysis.

The data of Table IV emphasize the fact that this catalyst is one of the most active known in promoting

TABLE IV

HYDROGENATIONS CATALYZED BY LITHIUM–ETHYLAMINE DERIVED CATALYST,[a] $ReO \cdot 2H_2O$

No.	Substrate[b]	Av. temp., °C.	Time, hr.	Product	Yield, %
1	Acetic acid (water)	145	4.5	Ethyl alcohol	100
2	Acetic acid	124	29	Ethyl alcohol	3
				Ethyl acetate	73
3	Propionic acid (water)	162	6	*n*-Propyl alcohol	100
4	Propionic acid	160	1	*n*-Propyl alcohol	25
				n-Propyl propionate	25
5	Isobutyric acid (water)	172	5	Isobutyl alcohol	95
				Isobutyl isobutyrate	5
6	Valeric acid (water)	168		Amyl alcohol	87
				Amyl valerate	13
7	Caproic acid (water)	177	3	*n*-Hexyl alcohol	73
				n-Hexyl caproate	27
8	Caprylic acid (water)	173	5	*n*-Octyl alcohol	100
9	Capric acid (water)	173	6	*n*-Decyl alcohol	100
10	Lauric acid (water)	177	7	*n*-Dodecyl alcohol	100
11	Benzoic acid (water)	198	10	Toluene	100
12	1-Phenyl-2-butene	171	2.5	Butylbenzene	100
13	Toluene	222	7	Methylcyclohexane	35
14	Pyridine (ethanol)	215	7	Piperidine	100
15	5-Hexen-2-one (ethanol)	68	10	2-Hexanone	91
16	5-Hexen-2-one (ethanol)[c]	155	2.5	2-Hexanone	14
				5-Hexen-2-ol	26
17	2-Allylcyclohexanone (ethanol)	125	6	2-Propylcyclohexanone	73
				2-Propylcyclohexanol	22
18	Crotonaldehyde (ethanol)	100	10	Butyraldehyde	50
19	Crotonaldehyde (ethanol)	140	20	*n*-Butyl alcohol	100
20	Nitrocyclohexane (ethanol)	120	7	Cyclohexylamine	100
21	Nitrophenylmethane (ethanol)	136	15	Benzylamine	20
				Nitrophenylmethane	16
22	*m*-Nitroacetophenone (ethanol)	110	24	*m*-Aminoacetophenone	100
23	*p*-Nitrophenylacetic acid (water)	157	2.5	*p*-Aminophenylacetic acid	61
				Polymer	39
24	*m*-Nitrostyrene (ethanol)	118	1	*m*-Aminostyrene	100
25	*m*-Nitrobenzaldehyde (ethanol)	124	10	*m*-Aminobenzaldehyde	100
26	Propargyl alcohol (ethanol)	142	2.5	Allyl alcohol	23
				n-Propyl alcohol	77

[a] Each run was made on 0.10 mole of substrate using 0.10 of g. catalyst. [b] Reaction solvent, if any, is indicated in parentheses. [c] In this run the catalyst was poisoned by the presence of a small amount of pyridine.

the hydrogenation of carboxylic acids to alcohols. Only the other rhenium oxide catalysts are comparable in catalytic activity.[19] The beneficial effect of water in this system in reducing side reactions is evident (**1–4**).

There are many examples illustrating the greater ease of hydrogenation of the olefinic bond in unsaturated carbonyl compounds than of the carbonyl bond (**21**, Table II; **4**, **5**, Table III; **15**, **17–19**, and **26**, Table IV). However, particular attention is directed to the *reversal* of this tendency when the catalyst was partially "poisoned" by a trace of pyridine (**15** and **16**, Table IV). This chance observation has not been further exploited.

A very great variation in the ease of reduction of different olefins is evident (*cf.* **2**, **4**, **5**, Table I; **20**, Table II; **2**, **3**, Table III; and **12**, Table IV). The complete selectivity of reduction of the side chain without accompanying reduction of the aromatic ring is evident.

Finally, attention is called to the relatively great resistance of nitro groups to hydrogenation by these rhenium catalysts compared with other reducible groups (Table I and **20–25**, Table IV). This peculiar phenomenon has been noted with other rhenium oxide catalysts in this series. However, in polyfunctional compounds containing the nitro group, the nitro group only is selectively reduced.

(19) *Cf.* ref. 2 and earlier papers in this series.