Rhenium Catalysts. IV.[1] Rhenium(III) Oxide from Perrhenate *via* Borohydride Reduction[2]

H. SMITH BROADBENT AND JOHN H. JOHNSON[3]

Department of Chemistry, Brigham Young University, Provo, Utah

Received May 15, 1962

The addition of sodium borohydride to cold aqueous solutions of perrhenate and acetic acid produces good yields of very finely divided, black rhenium(III) oxide possessing marked catalytic activity. A summary of some hydrogenations catalyzed by this substance is presented. The oxide is not ordinarily reduced to lower oxides or the metal during the process of hydrogenation.

Since the discovery of the complex metallic hydrides, most attention has been focused on their use in the reduction of organic compounds. Relatively little effort has been devoted to the reduction of metallic compounds with complex hydrides and only a small proportion of these metallic reduction products have been examined for activity in catalytic hydrogenations.[4]

Among the types of products obtained by the action of alkali metal complex hydrides on metallic salts are (1) the metathetical complex hydrides, (2) the free metals, (3) the simple metallic hydrides, (4) intermetallic compounds (*e.g.* nickel boride, Ni_2B), and (5) lower metallic oxides.[5-7]

The products of reduction of copper, cobalt, and nickel salts in aqueous solution by sodium borohydride have been shown to be hydrogenation catalysts, particularly when traces of chromium, molybdenum, or tungsten were present.[8]

Sodium borohydride is reported to be a good reducing agent for salts of nickel, ruthenium, tellurium, and rhenium.[9] No details and no mention of the use of these reduction products as hydrogenation catalysts are given.

It has now been shown that ammonium perrhenate can be reduced in an aqueous buffer of ammonium acetate and acetic acid by the addition of sodium borohydride to give excellent yields of rhenium(III) oxide. The rhenium(III) oxide obtained in this way can be isolated as a black, very finely divided powder by washing and centrifugation and stored by suspension in water. It is a very effective catalyst in the liquid phase hydrogenation of a variety of organic substrates under 125–300 atm. and 20–220°, using only 1 g. of rhenium/mole of substrate. The activity of the catalyst is moderately dependent on the detailed procedure used for its preparation.

The reduction of perrhenate by the hydride occurs at a negligible rate in water alone without the addition of acid. The use of too much acid results in a colloidal suspension from which the insoluble rhenium oxide cannot be isolated by centrifugation. The best yields of rhenium(III) oxide resulted when the molar ratio of ammonium perrhenate to sodium borohydride to acetic acid was 1:10–20:8–12. This obviously constitutes a large excess of borohydride over the stoichiometric ratio given by the equation:

$$2NH_4ReO_4 + NaBH_4 \longrightarrow Re_2O_3 + NaBO_2 + 2NH_4OH + H_2O$$

If the order of mixing the reactants is reversed so that the acetic acid–ammonium acetate mixture is added to the aqueous mixture of perrhenate and borohydride, consistently lower yields of a product having a lessened catalytic activity results.

Experimental

Preparation of Catalyst.—In a typical procedure a mixture of 2.04 g. (7.62 mmoles) of ammonium perrhenate,[10] 20 ml. (160 mmoles) of 8 N ammonium acetate solution and 2 ml. (35 mmoles) of glacial acetic acid dissolved in 100 ml. of water was cooled in an ice bath and vigorously stirred while a solution of 3.4 g. (90 mmoles) of sodium borohydride in 100 ml. of cold water was added dropwise over a 1-hr. period. When the borohydride addition was about one-half completed, an additional 2 ml. (35 mmoles) of acetic acid was added all at once. The mixture was stirred for 15 min. after the borohydride addition was completed and then centrifuged at full speed in a Servall SS-1 centrifuge. The supernatant solution was decanted, and the catalyst was washed twice by resuspension in distilled water followed by centrifugation. Finally the catalyst was resuspended in water and stored until time of use. The finely divided solid would remain in suspension for 12–24 hr.

---

(1) Part III of this series: H. Smith Broadbent, Graham C. Shaw, William J. Bartley, and John H. Johnson, *J. Org. Chem.*, **24**, 1847 (1959).

(2) This research was supported by Contract AF 18(600)-1164 with the U. S. 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 U. S. Government.

(3) This paper is based upon a thesis submitted by Mr. Johnson (1956) in partial fulfillment of the requirements for the degree of Master of Science, Brigham Young University.

(4) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956.

(5) H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra, and E. K. Hyde, *J. Am. Chem. Soc.*, **75**, 215 (1953).

(6) G. W. Schaeffer, J. S. Roscoe, and A. C. Stewart, *ibid.*, **78**, 729 (1956).

(7) O. Glemser, U. Hauschild, and O. Bimmerman, *Angew. Chem.*, **64**, 457 (1952).

(8) R. Paul, P. Buisson, and N. Joseph, *Compt. rend.*, **232**, 627 (1951); *Chem. Abstr.*, **45**, 10436 (1951).

(9) H. I. Schlesinger and H. C. Brown, U. S. Patent 2,461,661, (February 15, 1949). After this manuscript was submitted, the use of borohydride to reduce metal salts and subsequently to generate hydrogen for *in situ* hydrogenation was reported by H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, **84**, 1494 ff. (1962).

(10) Obtained from Prof. A. D. Melaven, Dept. of Chemistry, University of Tennessee, Knoxville, Tenn.

TABLE I

HYDROGENATIONS CATALYZED BY SODIUM BOROHYDRIDE PRODUCED RHENIUM(III) OXIDE

No.	Substrate	Solvent	Av. temp., °C.	Av. pressure, atm.	Time, hr.	Yield, %	Product(s)
1	Styrene	Ethanol	25	194	6	100	Ethylbenzene
2	Styrene	Ethanol	66	214	1.5	100	Ethylbenzene
3	*p*-Chlorostyrene	Ethanol	34	197	11	100	*p*-Chloroethylbenzene
4	1-Hexene	None	68	220	7	100	Hexane
5	2-Hexene	None	110	239	4	100	Hexane
6	Cyclohexene	Ethanol	100	242	3	86	Cyclohexane
7	2,4,4-Trimethyl-1-pentene	None	140	252	2.5	100	2,2,4-Trimethylpentane
8	Maleic acid	Water	100	238	8	100	Succinic acid
9	Maleic acid	Water	130	258	1	100	Succinic acid
10	Benzene	None	193	290	5	60	Cyclohexane
11	Benzene	Ethanol	284	359	2	48	Cyclohexane
12	Bromobenzene	None	265	335	5		No reduction
13	Naphthalene	Ethanol	250	354	6		No reduction
14	Pyridine	None	205	280	17	55	Piperidine
15	Butanone	None	72	217	3	100	2-Butanol
16	Butanone	Methanol	74	219	5	100	2-Butanol
17	3-Pentanone	Ethanol	90	220	4	89	3-Pentanol
18	Cyclohexanone	Ethanol	64	222	4.5	77	Cyclohexanol
19	Acetophenone[a]	Ethanol	150	255	1	100	Methylphenylcarbinol
20	Acetic acid	Water	155	258	13	65	Ethanol
						27	Ethyl acetate
21	Capronitrile	Ethanol	220	312	8	10	Hexylamine
						17	Dihexylamine
						25	Trihexylamine
22	Nitrobenzene	Ethanol	75	195	4	100	Aniline
23	*p*-Bromonitrobenzene	Ethanol	124	222	5.5	100	*p*-Bromoaniline
24	*m*-Nitroacetophenone	Ethanol	75	224	1.5		No reduction

[a] Only 0.5 g. of rhenium per mole of substrate.

Analysis of an aliquot of the original supernatant liquid for rhenium established that reduction to rhenium(III) oxide was 85% complete, giving a yield of 1.35 g. of catalyst. Yields by this procedure varied from 70 to 90%. Each batch of catalyst was checked for its ability to cause the hydrogenation of styrene at room temperature. All were able to do so in 6–10 hr.

Analysis of Catalysts.—Aliquot portions of stable aqueous suspensions of the catalyst were evaporated to dryness *in vacuo*, then heated *in vacuo* over phosphorus pentoxide at 150°, cooled in an atmosphere of nitrogen, and weighed. The samples were then dissolved in a mixture of 30% hydrogen peroxide and concentrated ammonium hydroxide, destroying excess peroxide by the addtion of urea. The perrhenate in solution was determined as the tetraphenylarsonium salt.[11]

Anal. Calcd. for Re_2O_3: Re, 88.8. Found: Re, 87.8; 89.6; 87.1; 88.2 (av. 88.2).

One sample of catalyst was analyzed following its use in the reduction of butanone. It contained 91% rhenium indicating little change during hydrogenation.

Hydrogenation Procedure.—Two-tenth mole of the compound being reduced, solvent (if any, as noted), and catalyst equivalent to 0.2 g. of rhenium were placed in a 420-ml. glass liner in a Parr Instrument Co. bomb rocking 36 times per minute. If the reaction solvent was not water, or if none was used, the water in which the catalyst was suspended was removed by centrifugation followed by decantation and then replaced by the reaction solvent, or substrate itself, if no solvent were used. Alternatively, when water-immiscible substrates were used the water was removed by azeotropic distillation. After adequate flushing to remove air, hydrogen was then added to a pressure of 3000 p.s.i.g. (204 atm.) The reactor was set to rocking and the rate of reaction noted by the fall in gage pressure. If the rate of hydrogenation was not immediately appreciable the temperature was raised in 40–50° increments, stopping agitation until the new temperature plateau was reached, until pressure drop was evident. The average pressures cited represent the pressure of the total system at the average temperature of hydrogenation. At the completion of reaction (as noted by pressure fall) the system was cooled and vented.

The filtered reaction product was analyzed by fractional distillation, chemical extraction, titration, and/or refractometry.

Purity of Substrates.—The compounds hydrogenated were of Eastman White Label grade or equivalent. The styrenes were freshly distilled before use to remove inhibitors added to prevent polymerization during storage.

Discussion of Results

A partial, but representative, sample of the catalytic hydrogenations carried out using rhenium(III) oxide prepared by the borohydride reduction of perrhenate is presented in Table I. In those cases where duplicate runs were made, the data were rather closely repeatable. It appears evident that the effective catalyst is the rhenium(III) oxide itself and not some reduction product, since elemental analysis of the catalyst recovered after completion of run no. 15 remained substantially unchanged from that initially introduced into the reacting system.

Attention may be directed to the following points: The carbon–carbon multiple bond is susceptible to reduction under conditions ranging from the room temperature hydrogenation of

---

[11] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, "Applied Inorganic Analysis," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 321.

styrene to the complete lack of hydrogenation of bromobenzene or naphthalene at *ca.* 350°. With the olefins the ease of hydrogenation (no. 4 > 5,7 < 6) appears to parallel the possession by the molecule in question of geometrical properties which most readily permit adsorption on the catalyst surface. The resistance of halogen substituents to hydrogenolysis by this catalyst (no. 3, 12, 23) is noteworthy. This property is shared by all rhenium catalysts we have studied. The marked effect of the solvent on the course of hydrogenation in some cases (no. 10, 11) and the absence of any significant effect in other cases (no. 15, 16) is interesting. This phenomenon has also been previously noted with other rhenium catalysts.

The carbonyl and nitro groups in separate molecules are relatively easily reduced, but the inclusion of both groups in the same molecule in the one case examined (no. 24) caused the nitro group to be resistant under conditions which would lead to easy hydrogenation otherwise.

The carboxylic acid group, which is hydrogenated with great difficulty if at all by most catalysts, is relatively easily reduced (no. 20). In this respect it is surpassed only by rhenium heptoxide reduced to the active catalyst *in situ.*[1]

Rhenium Catalysts. V. Rhenium Heptoxide–Tetrahydropyran Complex[1,2]

H. SMITH BROADBENT AND JOHN H. JOHNSON[3]

Department of Chemistry, Brigham Young University, Provo, Utah

Received May 15, 1962

Rhenium(VII) oxide reacts with boiling tetrahydropyran to form a nearly colloidal, black, voluminous, insoluble complex which has unusual activity in catalytic hydrogenations. It is relatively active in promoting saturation of aromatic hydrocarbons whereas nitro compounds are singularly inert under comparable conditions.

During an investigation of the solubility of yellow rhenium(VII) oxide in various solvents, it was observed that the oxide reacts readily with warm tetrahydropyran to form a very finely divided black, voluminous precipitate of rather indefinite composition containing 45 to 55% rhenium. The recovery of rhenium from tetrahydropyran in the form of this complex is 80–90%. This "black" is active in catalyzing the liquid phase hydrogenation of many organic compounds, particularly aromatic structures. On the other hand, nitro compounds are singularly inert to hydrogenation under these same conditions.

Nechamkin, Kurtz, and Hiskey[4] have reported that various ethers reduce rhenium(VII) oxide to rhenium(VI) oxide. In particular, dioxane forms a pearly-white crystalline complex having the composition $Re_2O_7 \cdot 3C_4H_8O_2$, which decomposes at about 145° giving a 40% yield of maroon-red rhenium(VI) oxide uncontaminated by lower or higher oxides.

The tetrahydropyran complex also decomposes on heating to form pure rhenium(VI) oxide. However, this oxide has a pattern of hydrogenation catalytic activity (to be reported in a subsequent paper of this series) entirely different from that of the black, undried, amorphous complex from which it is derived. The details of the preparation and catalytic activity of the tetrahydropyran complex are reported below.

Experimental

Rhenium(VII) oxide[5] was carefully ground to a fine powder in a mortar and pestle with strict exclusion of moisture. This substance appears to be even more hygroscopic than phosphorus(V) oxide.

Tetrahydropyran[6] was purified by extended refluxing over sodium metal ribbon followed by distillation. After a repetition of this process the distillate was stored over calcium hydride or sodium metal without discoloration occurring. It was filtered immediately prior to use.

Preparation of the Catalyst.—One and one-half grams of finely powdered rhenium(VII) oxide was added to 150 ml. of purified tetrahydropyran, and the mixture was refluxed 2 hr., cooled, and centrifuged. After decantation of the supernatant solvent, the very black, voluminous complex was washed with absolute ethanol by centrifugation and decantation and stored under absolute ethanol. The suspended complex settled very slowly. Air, water, or amines caused a change in color of the complex from black to caramel brown.

Analysis of the clear supernatant tetrahydropyran following centrifugation established that precipitation of the rhenium(VII) oxide as the tetrahydrofuran complex was 80–90% complete.

Analysis of Catalysts.—Samples were prepared for analysis in the same manner as reported in the immediately preceding paper of this series, except that it was sometimes necessary to filter off undissolved material after the initial treatment of the sample with concentrated ammonium hydroxide and 30% hydrogen peroxide and treat it again in order to dissolve it completely. The perrhenate ion was determined as its tetraphenylarsonium salt. Values for

---

(1) *Cf.* H. Smith Broadbent and John H. Johnson, *J. Org. Chem.*, **27**, 4400 (1962), for paper IV in this series.

(2) Support by the U. S. Air Force through their Office of Scientific Research, Contract AF 18(600)-1164 is gratefully acknowledged.

(3) This paper is based on a thesis submitted by Mr. Johnson (1956) in partial fulfillment of the requirements for the M.S. degree at Brigham Young University.

(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) Obtained as a massive yellow crystalline sublimate from Prof. A. D. Melaven, University of Tennessee, Knoxville, Tenn.

(6) Commercial material from the Electrochemicals Department, E. I. du Pont de Nemours, Inc.