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Rhenium and Its Compounds as Hydrogenation Catalysts. II. Rhenium Heptaselenide[1,2]

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The first recorded application of rhenium heptaselenide as a hydrogenation catalyst in the reduction of a variety of substrates is described. It is easily prepared and isolated and may be stored wet or dry in the presence of oxygen without loss of activity. Some further advantages enjoyed by rhenium heptaselenide as a catalyst are its extreme resistance to "poisoning," insolubility in strong non-oxidizing acids and ability to saturate multiple bond systems without accompanying carbon-to-sulfur bond hydrogenolysis.

One of the most common and bothersome (although sometimes helpful) phenomena in the area of contact catalysis is the strong and relatively irreversible chemisorption of some chemical species on the surface of the catalyst thus blocking the active sites thereon to the highly reversible adsorption–desorption processes associated with the usually desired reaction, *e.g.*, hydrogenation. This phenomenon is called "poisoning."[4] Among hydrogenation catalysts the most common of the three classes of poisons[5] are the elements themselves or molecules containing the elements of Groups Va and VIa in their "unshielded" forms, *i.e.*, having at least one pair of unshared electrons in their bonding orbitals which can enter into the unfilled *d* orbitals of the catalyst and hence become chemisorbed.

Compounds containing the highly polarizable sulfur atom in its bi-covalent state provide the most frequently encountered poisoning problem. Unfortunately, not only are traces of sulfur-containing impurities widely distributed, but frequently sulfur-containing compounds themselves must be hydrogenated. One means of avoiding this problem is the use of catalysts which are not subject to the strong chemisorption of these poisons, *e.g.*, the metallic sulfide catalysts.

There is no record in the chemical literature of the use of rhenium heptaselenide as the hydrogenation catalyst. In view of the outstanding properties of rhenium heptasulfide among sulfide catalysts in hydrogenation[1] and as a part of a systematic investigation of catalysis by rhenium compounds being made in this Laboratory, the properties of rhenium heptaselenide in catalyzing the hydrogenation of a variety of organic substrates in both the presence and absence of various catalyst "poisons" have been investigated.

Rhenium heptaselenide (accompanied by some free selenium) was easily prepared and isolated. In moderate amounts the free selenium (which is very difficult to remove completely) accompanying the catalyst preparation as a side reaction does no significant harm. Any adverse effects of relatively large amounts of it seem to be purely mechanical as shown by the studies related below (*cf.* Table II). The catalyst may be stored in an ordinary screw cap bottle undesiccated, in contact with air, with no significant loss in activity. It was not adversely affected by non-oxidizing acidic conditions. It was roughly comparable in catalytic activity to rhenium heptasulfide, being somewhat less active in most cases, but definitely superior in some. It was completely inert to poisoning by nitrogen, phosphorus, antimony, sulfur, selenium and tellurium in all cases tried (*cf.* Table III), being adversely affected only by arsenic and arsenic(III) oxide. Results obtained with the catalyst were readily duplicable. Those given below are representative.

Experimental

Experimental Preparation and Analysis of Rhenium Heptaselenide.—In a good hood hydrogen selenide was generated by heating powdered selenium and paraffin bath wax (melting at 60°) together in a ratio of *ca.* 1:3 by weight at 320–340° in a 1-l. round-bottom flask connected with ground glass semi-ball joints to a 400-cm. Vigreux column and thence through an empty trap to a mineral oil scrubber, and finally to a 1-l. gas absorption flask[6] containing 6.24 g. of potassium perrhenate and 6 g. of potassium hydroxide in 1 l. of water. The precipitation was usually complete in 8 hr. Rhenium heptaselenide prepared in this manner always contains some free selenium since the decomposition of hydrogen selenide is catalyzed by elemental selenium.

The virtually colloidal suspension resulting was very difficult to centrifuge or filter, but after coagulation with dil. hydrochloric acid it was filtered easily, although it was extremely voluminous, retaining much water. After drying *in vacuo* over phosphorus pentoxide, experiencing a fivefold reduction in volume, the product was pulverized and stored in a screw cap bottle. Occasionally the drying was omitted without ill effect where ethanol was used as the diluent in the hydrogenation reaction.

Analysis.—The catalyst was dissolved with 30% hydrogen peroxide in aq. ammonia solution. Since rhenium heptaselenide dissolved much more readily under these conditions than the free selenium, it was found possible to dissolve the rhenium heptaselenide only and determine the

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[1] Part I of this series: H. S. Broadbent, L. H. Slaugh and N. L. Jarvis, THIS JOURNAL, **76**, 1519 (1954).

[2] This work was performed under contract no. AF 18(600)-1164 with the U.S.A.F. Office of Scientific Research of the Air Research and Development Command.

[3] Abstracted from a thesis submitted in partial fulfillment of the requirements for the degree of Master of Science, 1956.

[4] P. H. Emmett, ed., "Catalysis," Reinhold Publishing Corp., New York, N. Y., 1954, Vol. 1, pp. 299–314.

[5] E. B. Maxted in "Advances in Catalysis," Academic Press, Inc., New York, N. Y., 1951, Vol. III, pp. 129–177.

[6] By accident one breath of hydrogen selenide diluted by air was inhaled. An immediate discharge of mucus and tears resulted, accompanied by severe irritation of eyes, nose, and throat. After 3 hr. breathing began to be difficult increasing in severity for several hours. A metallic taste persisted. By next morning symptoms bordering on pneumonia resulted—severe lung congestion, shortness of breath, especially painful spells of coughing. These symptoms rapidly subsided thereafter except that the metallic taste persisted for several days and the garlic-like odor of hydrogen selenide was noticeable on the breath for nearly two weeks. No impairment of the taste or olfactory senses was noticeable.

TABLE I

HYDROGENATIONS WITH RHENIUM HEPTASELENIDE CATALYST

No.	Substrate reduced[a]	Solvent	Avg. pressure, atm.	Avg. temp., °C.	Time, hr.	Yields, %	Product(s)
1	Nitrobenzene	Ethanol	240	155	1.25	100	Aniline
3	Nitrobenzene[b]	Ethanol	250	150	1.25	100	Aniline
4	Nitrobenzene[c]	Ethanol	242	110	1.25	100	Aniline
5	Nitrobenzene[d]	Ethanol	243	110	3.25	100	Aniline
8	Nitrobenzene	None	240	150	4.0	100	Aniline
9	Sodium *p*-nitrophenolate	Water	226	130	1.0	100	*p*-Aminophenol
11	1-Nitropropane	Ethanol	242	115	3.0	100	Propylamine
12	Hexene-1	None	285	205	0.5	57.5	Hexane
13	Hexene-2	None	272	200	.5	61.5	Hexane
14	2,4,4-Trimethylpentene-1	None	287	200	.5	93.5	Isoöctane
15	Cyclohexene	None	326	250	2.0	9.2	Cyclohexane
16	Cyclohexene	Ethanol	306	200	3.0	40.0	Cyclohexene
17	Styrene	Ethanol	246	135	2.0	94	Ethylbenzene
18	Allyl alcohol	None	258	150	1.0	100	1-Propanol
19	Crotonic acid	Water	262	150	8.0	100	Butyric acid
20	Maleic acid	Water	207	60	7.0	100	Succinic acid
21	Maleic acid	*p*-Dioxane	265	150	0.75	100	Succinic acid
22	Cinnamic acid	*p*-Dioxane	260	145	2.5	100	Hydrocinnamic acid
23	Sodium cinnamate	Water	278	140	8.5	...	Unreacted starting material
25	Allyl phenyl sulfide	Ethanol	292	195	2.0	100	*n*-Propyl phenyl sulfide
26	Phenylacetylene	Ethanol	268	100	1.0	73.6	Ethylbenzene
						26.4	Polymer
27	Benzene	Ethanol	332	240	62.5	4.5	Cyclohexane
28	Thiophene	None	322	250	13	100	Thiolane
30	Quinoxaline	Ethanol	264	155	2.0	65	Tetrahydroquinoxaline
32	Amyl cyanide	Ethanol + NH_3	265	150	1.5	72	Hexylamine
						18.5	Dihexylamine
						2.5	Trihexylamine
33	Butanone	None	238	105	5.0	100	Butanol-2
34	Cyclohexanone	Ethanol	266	155	9.0	100	Cyclohexanol
35	Acetophenone	Ethanol	248	150	2.25	88	Ethylbenzene
						10	Methylphenylcarbinol
36	Acetic acid	None	314	210	11.0	56	Ethyl acetate
						14	Ethanol
						30	Unidentified
37	*p*-Nitrobromobenzene	Ethanol	235	100	3.0	100	*p*-Bromoaniline
38	Bromobenzene	None	301	195	3.0	22	Benzene
						78	Bromobenzene
39	Dimethylphenylcarbinol	Ethanol	264	160	1.1	100	Cumene
40	Benzyl phenyl sulfide	Ethanol	326	190	7.0	100	Benzene
						100	Benzyl mercaptan
41	Diphenyl disulfide	Ethanol	377	240	4.0	33	Diphenyl disulfide
						66	Benzene

[a] The amount of catalyst used was 2.5 g./mole of substrate in every case. This catalyst as prepared contained *ca.* 0–5% free selenium. [b] Catalyst was dried *in vacuo* over phosphorus pentoxide just prior to use. [c] Catalyst extracted with chloroform for 24 hr. to remove free selenium. [d] Catalyst extracted with toluene for 40 hr. to remove free selenium.

free selenium from the undissolved residue. With higher peroxide concentration, both would dissolve. The rhenium was determined as the tetraphenylarsonium perrhenate and the selenium as the metal after reduction.[7]

Anal. Calcd. for Re_2Se_7: Re, 40.4; Se, 59.6. Found: Re, 40.8; Se, 59.2; free selenium accompanying this sample, 3.8%; material balance, 99.8% (Se + Re_2Se_7).

Hydrogenation Procedure.—The compound to be reduced (usually 0.1 mole), the solvent or diluent if any (usually ethanol), and the catalyst (in every case 2.5 g./mole substrate, *i.e.* <1.0 g. Re/mole substrate), all in a glass liner, were placed in the hydrogenation bomb under an initial pressure of 204 atm. of hydrogen. Most reductions were run in an 550-ml. Aminco rocking type bomb with a fixed rocking speed of 37 cycles/min. In some cases either an Autoclave Engineers "Magne-Dash" 250 ml. unit with a variable rate of churning action operated at *ca.* 35–40 cycles/min. or a Parr Instrument Co., 1000-ml. unit with a fixed rocking rate of 37 cycles/min. were used. Under the conditions studied the course of a given reaction did not appear to be significantly affected by the reaction vessel chosen.

In order to obtain minimal conditions for the reaction, agitation was maintained for some time at room temperature and then raised in approx. 50° increments until an appreciable rate of pressure drop was discernible. The reactors were equipped for simultaneous recording of both temperature and pressure so that the average conditions prevailing during the actual reduction of the compound could be graphically determined.

Analysis of Reaction Products.—The diluent, if any, was removed by distillation and the residue analyzed by fractional distillation, extraction or precipitation, and refractometry.

Studies on Influence of Removal of Free Selenium from the Catalyst.—A batch of catalyst was prepared allowing the hydrogen selenide to bubble through the perrhenate solution

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(7) Hillebrand, Lundell, Bright and Hoffman, "Applied Inorganic Analysis," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 321 and 335, respectively.

for a long period after rhenium heptaselenide precipitation was complete. In this way a product resulted containing 50% free selenium, 50% rhenium heptaselenide. This was divided into ten 1-g. portions, one of which was retained as a control and the remaining portions extracted for varying periods of time in Soxhlet extractors with either chloroform or toluene as shown in Table II. Then each portion was analyzed and its catalytic activity evaluated by measuring its effectiveness in the hydrogenation of nitrobenzene.

Studies on Catalyst Poisoning.—Hydrogenations of nitrobenzene were made with 2.5 g. of the catalyst/mole of substrate with the addition in each case of an amount of the "poison" equal to the weight of catalyst used. The lack of reduction to aniline was taken as a measure of poisoning. Results are given in Table III.

Discussion of Results

The results given in Table I are representative of the catalytic properties of rhenium heptaselenide in a variety of hydrogenation reactions.

Rhenium heptaselenide was found to be comparable to but somewhat less active than rhenium heptasulfide against most substrates but decidedly superior to molybdenum sulfides or cobalt polysulfide. If free selenium was present in the catalyst, some conversion to hydrogen selenide occurred during hydrogenation conditions; however, after removal of free selenium, the rhenium heptaselenide was completely stable to change under the conditions studied.

The data on nitrobenzene show that using the rhenium selenide as usually prepared, *i.e.*, with a small amount (<5%) of free selenium present, removal of the free selenium by extraction improved the ease of reduction slightly. The effect of drying the catalyst was not significant.

Data on nitrobenzene and cyclohexene show that the catalyst was more efficient when ethanol was used as a diluent.

In contrast to the behavior of most hydrogenation catalysts the carbon–oxygen double bond was more easily saturated than the carbon–carbon double bond except where the latter was conjugated with other multiple bonds.

Attention is directed especially to the hydrogenation of acetic acid under relatively mild conditions and to the hydrogenation of the carbon–carbon double bonds in thiophene and in allyl phenyl sulfide without accompanying carbon–sulfur bond scission.

Hydrogenolysis of the carbon–halogen bond does not occur readily. The benzene ring was very resistent to hydrogenation. The nitrile function was relatively easily reduced.

The data given in Table II show the curious phenomenon that when rhenium heptaselenide contaminated with a large excess (50%) of free selenium was initially extracted with chloroform or toluene, its activity dropped very markedly. Then as successive amounts of selenium were removed by further extraction, the catalyst activity gradually improved. This suggests that the effect of the selenium originally co-precipitated with the rhenium heptaselenide is purely mechanical and has no direct effect on catalyst activity, but that during the process of extraction selenium is deposited from solution onto the surface of the rhenium heptaselenide lattice thus reducing the activity of the latter. The activity is then gradually restored as the selenium is removed by further extraction.

TABLE II

INFLUENCE OF REMOVAL OF FREE SELENIUM FROM RHENIUM HEPTASELENIDE

Extraction solvent	Extraction time, hr.	Analysis of catalyst[a] Re, %	Se, %	Catalyst[b] evaluation
Unextracted	..	19.6	80.1	34.7
Chloroform	5	22.7	77.8	1.3
Chloroform	10	24.1	75.1	11.8
Chloroform	20	26.9	73.3	16.0
Chloroform	40	28.8	71.4	19.7
Chloroform	100	33.5	66.3	30.2
Toluene	5	20.7	79.3	6.4
Toluene	10	21.5	78.0	9.0
Toluene	20	24.0	75.9	11.8
Toluene	40	25.2	74.8	13.0

[a] Includes free and combined selenium. Calcd. for Re_2Se_7: Re, 40.1; Se, 59.6. [b] Expressed as percentage conversion of nitrobenzene to aniline effected in a 1-hr. period at 100°, 2.5 g. of catalyst/mole, 200 atm. initial hydrogen pressure.

The data of Table III demonstrate the extreme resistance of the rhenium heptaselenide catalyst to "poisoning" by elements of groups Va and VIa, except arsenic.

TABLE III

HYDROGENATIONS OF NITROBENZENE WITH RHENIUM HEPTASELENIDE IN THE PRESENCE OF VARIOUS GROUP Va AND VIa ATOMS[a]

Catalyst "poison"	Avg. pressure, atm.	Avg. temp., °C.	Time, hr.	Yield, % aniline
None	236	100	1.0	100
Quinoline	235	112	2.2	100
Sodium hypophosphite	240	110	1.5	100
Arsenic(III) oxide	272	150	3.5	11
Arsenic	257	110	7.5	0
Antimony	236	112	1.5	100
Sulfur	236	105	1.5	100
Selenium	237	120	1.0	100
Tellurium	241	115	1.3	100

[a] In each case 2.5 g. of catalyst and 2.5 g. of the poison per mole of nitrobenzene was used. Ethanol was the reaction solvent.

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