Studies on the Silk-Rhodium Catalyst

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A series of the hydrogenation catalysts, composed of highly dispersed metal on fibers of silk fibroin, has recently been studied. The silk-palladium(1) and silk-platinum(2) catalysts, have shown a number of interesting properties that probably depend upon the nature of the carrier silk-fibroin fibers. In particular, catalysts of this type are highly selective with respect to the reactions that they catalyze. The metal used in the present study was rhodium which was recently found to be an excellent catalyst for the reduction of aromatic or heterocyclic double bond. The silk-rhodium catalyst was prepared by boiling silk-fibroin fibers with an aqueous solution of rhodium chloride and then hydrogenating the resulting silk-$RhCl_3$-complex.

The silk-palladium catalyst selectively hydrogenated the C=C double bond without reducing

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1) For example, S. Akabori, S. Sakurai, Y. Izumi and Y. Fujii, *Nature*, **178**, 323 (1956); Y. Izumi, This Bulletin, **32**, 932, 936, 942 (1959).

2) A. Akamatsu, Y. Izumi and S. Akabori, ibid., **34**, 1067 (1961); ibid., **34**, 1302 (1961).

the carbonyl group in an aliphatic molecule, which contains both groups. In the case of silk-rhodium catalyst, it appears that the selectivity was much increased. In the present work, it was found that this catalyst easily catalyzes the hydrogenation of $C{=}CHCH_2OH$ and $C{=}CHCOOH$ type of the C=C double bonds, while carbonyl groups, including those of aromatic compounds, could not be hydrogenated at all. This catalyst was relatively less active for the hydrogenation of the other type of the C=C double bonds, such as $C{=}CHCO{-}R$, and of nitro groups.

Results and Discussion

Conditions for Preparation of the Catalysts. — In order to obtain a catalyst with high activity and to minimize expensive loss of rhodium, optimal conditions were sought for the preparation of the silk-rhodium chelate and for the activation of the resulting chelate to the catalyst.

In Fig. 1a the rhodium contents in the chelate prepared in the different preparations are shown: when 400 mg. of silk-fibroin fibers were boiled with an aqueous solution containing 100 mg. of rhodium chloride ($RhCl_3$) for 25 min. The concentration was varied by changing the volume of water, and maximum chelation occurred in a mixture containing 100 mg. of silk-fibroin fibers in 0.5% aqueous $RhCl_3 \cdot H_2O$.

The optimal volume of the 0.5% $RhCl_3$ solution and boiling time was then determined. The results are summarized in Figs. 1b and 1c. Two hundred milligrams of each of the resulting chelate was activated by reduction in an autoclave, with ca. 90 kg./cm^2 of hydrogen in 50 ml. of water at 160°C for 1.5 hr., and the activities of the obtained catalysts were measured. The activity yield ($y \cdot v$), the product of the reaction velocity (v) and gravity yield (y)2) is a measure of activity of the catalyst for a given amount of the metal in the catalyst. Reaction velocity (v) was measured during hydrogenation of allyl alcohol to propyl alcohol with the same amount of catalyst, and was calculated by the equation; $v=100/t$, where t is the time in minutes required for 70% uptake of hydrogen.

As can be seen from data described here, the most favorable result was obtained, when 400 mg. of silk-fibroin fibers were boiled with 30 ml. of a 0.5% aqueous solution of rhodium chloride for ca. 30 min. The obtained silk-rhodium chelate consisted of golden-colored fibers which contained approximately 3.6% of the metal. This preparation was used for the work described in the following section of this paper.

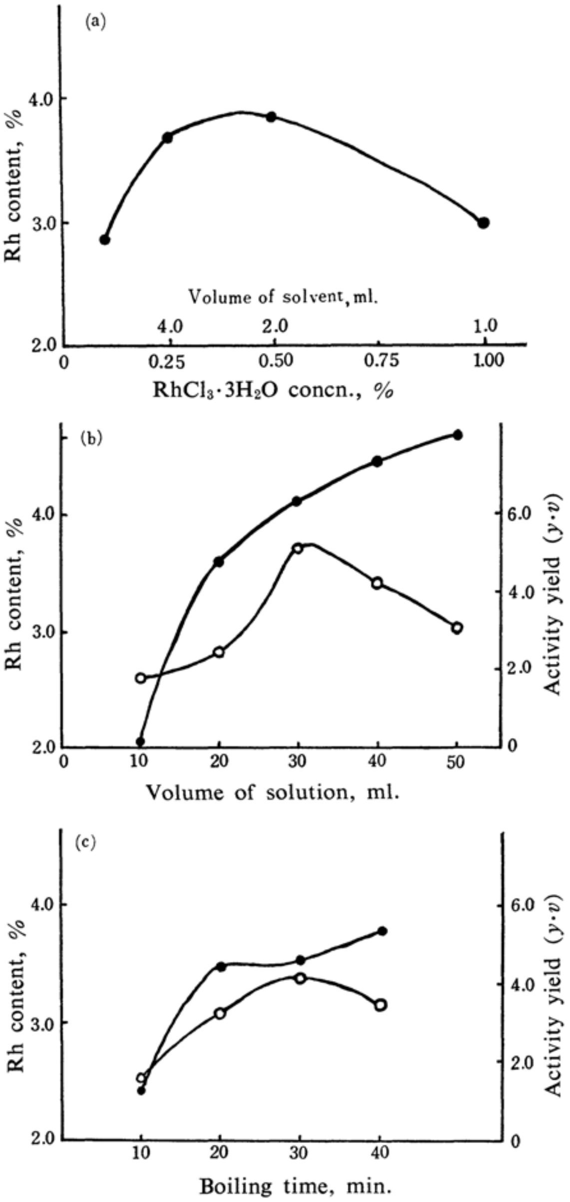

Fig. 1. Rhodium content of chelate under various conditions and activity yield of activated catalyst.

● Rhodium content

○ Activity yield

Silk-fibroin 400 mg. was boiled (a) in an aq. solution containing 100 mg. of $RhCl_3 \cdot 3H_2O$ for 25 min., (b) in a 0.5% $RhCl_3 \cdot 3H_2O$ aq. solution for 25 min., and (c) in 30 ml. of the solution.

Table I is a summary of experiments in which chelate was activated by reduction in an autoclave with ca. 90 kg./cm^2 of hydrogen in 50 ml. of water at various temperatures for different periods. The activity of the obtained catalyst, represented by the reaction

TABLE I. ACTIVITY OF THE CATALYST PREPARED UNDER VARIOUS CONDITIONS

No.*	Precursor chelate, mg.	Temp. °C	Time hr.	Grav. yield y, %	React. vel. at 32°C, v	Act. yield $y\cdot v$
a -1	200	100	2	82	5.3	4.3
a -2			3	89	6.6	5.9
a -3			4	82	8.0	6.6
a -4			5	86	6.8	5.8
a -5		120	2	78	5.2	4.1
a -6			3	81	5.7	4.6
a -7			4	77	5.8	4.5
a -8			5	70	3.1	2.2
a -9		140	1	73	6.6	4.8
a -10			2	68	5.8	3.9
a -11			3	63	5.6	3.5
a -12			4	65	6.9	4.5
a -13		160	1	56	12.7	7.1
a -14			2	57	11.3	6.4
a -15			4	51	11.2	5.7
b -1	200	140	3	63	7.6	4.8
b -2	1000	140	3	57	8.3	4.7
b -3	200	160	2	31	15.0	4.7
b -4	1000	160	2	31	15.5	4.8

* a differs from b in lot of the chelate prepared.

velocity (v) and the activity yield ($y\cdot v$) during the hydrogenation of allyl alcohol to propyl alcohol, was as dependent upon the temperature and time of activation as that of the silk-platinum catalyst. Increasing the amount of the precursor chelate used with respect to the amount of the solvent (water) did not influence the activity.

Stability of the Catalyst.—The reaction velocities measured by the method described above are shown in Table II. The catalyst was used both immediately after its activation and after it was dried and stored for several days in a stopped bottle. Storage of the catalyst for a long period resulted in considerable increase of activity.

TABLE II. STABILITY OF CATALYST

Storage time days	React. vel. at 32°C, v
1	8.8
3	8.5
8	15.2
15	14.2
47	9.0

The activity of the silk-rhodium catalyst was strongly inhibited by some substances. The inhibitory effects of certain poisons on the hydrogenation of 0.1 mol. of allyl alcohol in methanol in the presence of 20 mg. (containing ca. 10^{-5} mol. of Rh) of the catalyst was investigated. The results are shown in Table III. The behavior of this catalyst towards metal ions was similar to that of the silk-platinum catalyst. It was found that silk-rhodium catalyst poisoned with both ferric and cupric ions could be reactivated by treatment with ethylenediaminetetraacetic acid (EDTA).

Acetylation of this catalyst scarcely affected the activity. The reaction velocity (v), as defined above, with an acetylated catalyst was 10.4 at 32°C.

TABLE III. POISONING OF CATALYST

	Addition $\times 10^{-6}$ mol.	React. vel. at 32°C, v
PhCH$_2$SH	None	9.0
	1	4.4
	2	3.4
	3	0.1
Fe(NO$_3$)$_3$·12H$_2$O	10	1.9
	(treated with EDTA)*	4.4
	50	1
Cu(NO$_3$)$_3$·3H$_2$O	50	5.0
	200	5.0
	410	2.7
	440	1.8
	460	0.5
	(treated with EDTA)**	2.7

* 75% of the catalyst was recovered and treated with EDTA.

** 56% of the catalyst was recovered to be treated.

TABLE IV. CATALYTIC REDUCTIONS OF VARIOUS COMPOUNDS

Substrate g.	Solvent ml.	Cat. mg.	Temp. °C	H_2-Uptake %	Time min.	Product	Yield %
Acetaldehyde (11)		50	40	3	390	—	—
Benzaldehyde (25)		50	10	9	390	—	—
Benzaldehyde (25)		50	80	6	215	—	—
Ethyl methyl ketone (36)		200	80	2	390	—	—
Allyl alcohol (5.8)		20	16	100	37	Propanol	100*
Maleic acid (11.6)	MeOH(50)	20	55	100	74	Succinic acid	62
Diethyl maleate (34.5)		40	11	8	300	—	—
Diethyl maleate (34.5)		40	45	9	330	—	—
Cinnamic acid (7.4)	MeOH(50)	10	10	100	160	2-Phenylpropionic acid	87
Cinnamic acid (3.7)	aq. NaOH(50)	10	9	100	320	2-Phenylpropionic acid	72
Acrolein (5.6)	EtOH(50)	20	17	100	250	Propionaldehyde	93*
Crotonaldehyde (14)	MeOH(50)	40	15	18	350	—	—
Cinnamaldehyde (13)	MeOH(50)	20	15	9	210	—	—
Mesityl oxide (24.5)		50	55	20	270	Isobutyl methyl ketone	20*
2-Butyne-1,4-diol (4.3)	MeOH(50)	20	19	100	245	1,4-Butanediol	100
Nitrobenzene (4)	MeOH(50)	40	10	10	330	—	—
Nitrobenzene (4)	MeOH(50)	40	90	88	300	Aniline	60**
p-Nitrotoluene (4.6)	MeOH(50)	40	90	100	30	*p*-Toluidine	70**
Nitromethane (6.1)	Ac_2O(50)	60	50	2	250	—	—
Diethyl nitromalonate (4.2)	Ac_2O(50)	20	40	8	128	—	—
m-Nitrocinnnamic acid (4.8)	aq. NaOH(50)	10	70	80	100	*m*-Aminocinnamic acid *m*-Amino-2-phenylpropionic acid	29 29

* Estimated directly by gas-chromatography of the reaction mixture.

** Estimated by isolating the products as *N*-acetyl derivatives.

Selectivity of the Catalyst.—The catalytic efficiency of the silk-rhodium catalyst on various substrates was examined. For each mole of hydrogen required for complete reduction, 200 mg. of the catalyst were used under ca. 90kg./cm^2 of hydrogen in a 100 ml. autoclave. The results are summarized in Table IV.

In an earlier study it was observed that hydrogenation of both acetaldehyde and benzaldehyde did not take place in the presence of a silk-platinum catalyst, when hydrogen was introduced into the reaction vessel before the reactant had been heated to a reaction temperature; however, when catalyst and aldehyde were pre-heated and then hydrogen was introduced, the reaction occurred. All the compounds tested in the present work, were heated before introduction of hydrogen.

Hydrogenation of the Carbonyl Group.—In the presence of this catalyst the carbonyl group was not hydrogenated in any of the aldehydes and ketones listed in the Table IV.

Hydrogenation of the C=C Double Bonds.—This catalyst is extremely active in hydrogenating C=C double bonds in compounds of the types $C=CHCOOH$ and $C=CHCH_2OH$, such as allyl alcohol, maleic acid, and cinnamic acid. On the other hand, the hydrogenation of the C=C double bonds attached to an ester group or conjugated with a carbonyl group seems to be difficult with this catalyst, and hydrogen uptake by diethyl maleate, cinnamaldehyde and crotonaldehyde was very low. Mesityl oxide absorbed a small amount of hydrogen, yielding only isobutyl methyl ketone, and preserving its carbonyl group intact. The C=C double bond in acrolein, which is conjugated with carbonyl group, behaved typically in that it could be easily hydrogenated at low temperature. The carbonyl group was not attacked, and propionaldehyde was produced in a nearly quantitative yield.

Thus it appears that the silk-rhodium catalyst is capable of easily catalyzing the hydrogenation of the aliphatic C=C double bonds in some molecules leaving unaltered their coexisting carbonyl groups. The double bonds in benzene rings were not hydrogenated in the presence of this catalyst.

Reduction of Nitro Groups.—The hydrogenating activity of silk-platinum catalyst was reported to be extremely high for nitro groups attached to aromatic rings and low for aliphatic nitro groups and C=C double bonds. In the present work, however, the catalyst showed comparatively little activity in the hydrogenation of aromatic nitro groups, and the aliphatic nitro groups of nitromethane and diethyl nitromalonate were not reduced at all in the presence of acetic anhydride.

Nitrobenzene was not reduced except at high temperature, but the substituted nitrobenzenes, *p*-nitrotoluene and *m*-nitrocinnamic acid, were easily reduced.

2-Butyne-1, 4-diol.—It was easily hydrogenated to give 1, 4-butanediol quantatively.

Experimental

Determination of Rhodium.—Rhodium was determined by the stannous iodide method[3], after the chelated sample had been treated as follows; about 25 ml. of the chelated sample was accurately weighed in a test tube and heated with 0.5 ml. of concentrated nitric acid on a steam bath for 1 hr. The mixture was diluted with 4 N hydrochloric acid to 50.0 ml. Exactly 5.00 ml. of the solution was used for each ascertainment.

The standard curve was made with a solution containing accurately weighed rhodium chloride trihydrate to which was added a certain amount of silk-fibroin decomposed by the method described above for the chelated sample.

Measurement of the Reaction Velocity.—Twenty milligrams of the catalyst to be tested and 5.8 g. (0.1 mol.) of allyl alcohol dissolved in 50 ml. of methanol were placed in a 100 ml. autoclave. Hydrogen was then introduced to a pressure of 90 kg./cm^2, and the time required for 70% of the theoretical hydrogen uptake measured.

Preparation of Catalyst. — Five grams of the silk-rhodium chelate prepared as described previously were reduced in a 300 ml. autoclave with 90 kg./cm^2 of hydrogen in 150 ml. of water, at 140°C for 3 hr. The catalyst obtained was washed with water, methanol, and ether in succession, and then dried in vacuo; yield: 3.2 g. (65%), rhodium content: ca. 5.4% (calculated from rhodium content in the precursor chelate and the yield).

Treatment of the Inhibited Catalysts by Ethylenediaminetetraacetic Acid (EDTA). — The inhibited catalyst was boiled with 100 ml. of 0.5% aqueous solution of EDTA for 5 min., filtered, washed with water, methanol and ether, and finally dried in vacuo.

Acetylation of the Catalyst.—One hundred milligrams of the catalyst were boiled with 50 ml. of acetic anhydride for 2 hr., filtered, washed with ether, and dried in vacuo. The activity of this catalyst was measured by the same procedure used in testing nonacetylated catalyst.

Isolation of the Product.—*Hydrogenation of Allyl Alcohol, Acrolein and Mesityl Oxide.*—The reaction mixture was filtered and the filtrate was treated by gas chromatography; the products were identified as propyl alcohol, propionaldehyde, and isobutyl methyl ketone, respectively, and the yield estimated.

Hydrogenation of Maleic Acid.—The reaction mixture was filtered, the filtrate evaporated to 20 ml., and to this was added 20 ml. of water. After standing overnight, 3.7 g. of succinic acid (m. p. 179∼181°C) was obtained. It was confirmed by infrared spectroscopy that the product had no unsaturated bond.

Found: C, 41.25; H, 5.17. Calcd. for $C_4H_6O_4$: C, 40.68; H, 5.12%.

Hydrogenation of Cinnamic Acid.—(i) The reaction mixture was filtered, the filtrate evaporated to 10 ml., and to this was added 20 ml. of 1 N hydrochloric acid. After standing in a refrigerator overnight, 6.4 g. of 2-phenylpropionic acid (m. p. 47.5°C) was obtained.

Found: C, 72.36; H, 6.74. Calcd. for $C_9H_{10}O_2$: C, 72.98; H, 6.71%.

(ii) An aqueous solution of cinnamic acid adjusted to pH 7.0 with sodium hydroxide, was subjected to hydrogenation. The reaction mixture was evaporated to 20 ml., and then acidified with 15 ml. of 2 N hydrochloric acid. After standing in a refrigerator overnight, 2.7 g. of 2-phenylpropionic acid (m. p. 49°C) was obtained.

Found: C, 72.15; H, 6.62. Calcd. for $C_9H_{10}O_2$: C, 71.98; H, 6.71%.

These products were proved to have no unsaturated bond, by infrared spectroscopy.

Reduction of Nitrobenzene and p-Nitrotoluene.—After filtration of the reaction mixture 10 g. of acetic anhydride was added to the filtrate. It was evaporated to dryness and the residue treated with a small amount of water. After standing 2.7 g. of acetanilide (m. p. 113∼115°C) and 3.5 g. of *p*-acetotoluidide (m. p. 149°C) was obtained from aniline and *p*-toluidine, respectively.

Acetanilide. Found: N, 10.30. Calcd. for C_8H_9NO: 10.37%.

p-Acetotoluidide. Found: N, 9.28. Calcd. for $C_9H_{11}NO$: 9.39%.

Reduction of m-Nitrocinnamic Acid.—The reaction mixture was evaporated, and to this was added 25 ml. of 2 N hydrochloric acid. Obtained precipitate was filtered off, washed with water and dried in vacuo. (Dried weight, 800 mg.). The fiiltrate was concentrated to 50 ml., to the residue was added 2.5 g. of acetic anhydride and 2 g. of sodium acetate, and the mixture was stirred for 3 hr. Then, a mixture of *m*-acetaminocinnamic acid and 2-*m*-acetaminophenylpropionic acid was precipitated. *m*-Acetaminocinnamic acid content was estimated to be 49.5% by measuring hydrogen uptake on further hydrogenation of this mixture in methanol with Pd-C catalyst.

The mixture. Found: C, 63.15; H, 6.21; N, 6.83. Calcd. for $C_{11}H_{13}O_3N+C_{11}H_{11}O_3N$ (1 : 1): C, 64.07; H, 5.68; N, 6.80%.

Hydrogenation of 2-Butyne-1, 4-diol.—After filtration of the reaction mixture, the solvent was removed from the filtrate by evaporation, and the residue was dried in vacuo. The product was identified as 1, 4-butanediol by infrared spectroscopy.

Summary

1) The most active catalyst was obtained when 400 mg. of silk-fibroin was boiled with 30 ml. of 0.5% aqueous solution of rhodium chloride for ca. 30 min., and the resulting chelate was then reduced.

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[3] E. B. Sandell, "Colorimetric Determination of Traces of Metals", Interscience Publishers, New York (1959), p. 774.

2) The activity of this catalyst was not influenced significantly by the conditions for its preparation and was maintained or even increased greatly on storage for a long period. Benzyl mercaptan, ferric and cupric ions poisoned the catalyst, but the inhibition by the metal ions could be restored by ethylenediaminetetraacetic acid.

3) This catalyst was extremely active for the hydrogenation of the types C=C double bonds $C=CHCH_2OH$ and $C=CHCOOH$ but inactive for carbonyl groups. For the hydrogenation of other types of C=C double bonds and of nitro groups, the catalyst seems to be less active.

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