Reduction of Organic Compounds with Urushibara Catalysts under High Pressure. X[1)]. Hydrogenation of 2-Butyne-1,4-diol to cis-2-Butene-1,4-diol with Various Urushibara Catalysts

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In the previous paper[1)] of this series, the catalytic reduction of some carbonyl compounds with various Urushibara catalysts was reported. Since the discovery of the Urushibara nickel catalyst[2)], the preparation of the catalyst has been successively modified and some varieties of the nickel catalysts, U-Ni-B[1-5)], U-Ni-BA[6,7)], U-Ni-NH_3[8)], U-Ni-CB[5)], U-Ni-A[1,4,5,9,10)], U-Ni-AA[11)], U-Ni-CA[5)] and U-Ni-A(HCl)[1)], have been furnished. Besides these nickel catalysts, some Urushibara cobalt and copper catalysts, namely, U-Co-B[5,8,12,13)], U-Co-CB[5)], U-Co-A[5,13)], U-Co-CA[5)], U-Cu[5)] and U-Cu-C[1,5)], have been reported on. As each of them has its own characteristics and proper activity, one can choose a catalyst in accordance with the compound to be reduced.

In the present paper, the hydrogenation of 2-butyne-1, 4-diol with some Urushibara catalysts is studied.

Experimental

Apparatus.—Hydrogenation was carried out in an electro-magnetically stirring-type autoclave with a capacity of 100 ml. (Sakashita SE-10).

2-Butyne-1, 4-diol.—A commercially available crude sample was recrystallized from benzene, m.p. 58.5°C.

General Procedure for Hydrogenation.—The catalyst was carefully transferred with ethanol into the autoclave. The air in the autoclave was replaced by hydrogen gas four times. Most operations were carried out under the following conditions: (1) sample; 4.3 g. (0.05 mol.) (2) solvent; ethanol (99%) 50 ml. (3) agitation; 40∼45 strokes per minute. Agitation was started when the temperature in the autoclave reached the reaction temperature. (4) pressure; Initial pressure was chosen to be above 50 kg./cm². Depression of the pressure was observed at intervals of five minutes.

Hydrogenation Products.—*cis-2-Butene-1, 4-diol.*—After the hydrogenation was finished, the catalyst was filtered off and washed with ethanol. The major part of the solvent was distilled off from the combined solution, and the residual liquid was distilled under reduced pressure. *cis*-2-Butene-1,4-diol was obtained as a colorless oil, b. p. 125∼126°C/12 mmHg. Yield, 70∼75% of the theoretical. The dibenzoate crystallized into colorless prisms from ethanol, m. p. 67∼68°C.

1, 4-Butanediol.—After removal of the catalyst, the product was distilled to give 1,4-butanediol as a colorless oil, b. p. 131∼132°C/25 mmHg. Yield, 73% of the theoretical. The dibenzoate crystallized into colorless prisms from ethanol, m. p. 82.5∼83.5°C.

Preparation of Catalysts.—The U-Ni-A(s)*(HCl) was prepared by the method described in the reference cited[1)]. Some new Urushibara catalysts were prepared by the methods described below. The U-Fe-BA was also prepared from ferric chloride and aluminum grains in the same way as the U-Ni-BA, but it was found to be inactive.

a) Urushibara Iron Prepared from Ferric Chloride, Abbreviated as U-Fe(III).—To a well mixed zinc dust (25 g.) and water (8 ml.) placed in a 50 ml. beaker, 9.68 g. (containing 2 g. of iron) of the crystal of commercially available ferric chloride ($FeCl_3 \cdot 6H_2O$) was added. The mixture was then well stirred with a glass rod. Soon a vigorous exothermic reaction started, but it subsided within about ten seconds. To complete the reaction the mixture was stirred until the color of the ferric ion disappeared. The reaction mixture (precipitated iron) was washed with 400 ml. of cold water, and then the washing was removed by filtration or decantation. The precipitated iron was digested in 330 g. of 15% acetic acid with occasional stirring at 60∼70°C for about 20∼25 min. At the end of the digestion, the generation of hydrogen gas subsided, and a solid, adsorbing hydrogen gas came up to the surface of the almost colorless solution. The solid was quickly collected on a glass filter and washed with 300 ml. of cold water and then

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1) Part IX; S. Taira, This Bulletin, **34**, 1294 (1961).
2) Y. Urushibara, ibid., **25**, 280 (1952).
3) Y. Urushibara and S. Nishimura, ibid., **27**, 480 (1954).
4) Chem. Soc. Japan, ed., "Jikken Kagaku Kōza", Vol. 17, Part 2, Maruzen, Tokyo (1956), p. 311.
5) S. Taira, This Bulletin, **34**, 261 (1961).
6) K. Hata, S. Taira and I. Motoyama, ibid., **31**, 776 (1958).
7) I. Motoyama, ibid., **33**, 232 (1960).
8) S. Nishimura and A. Sugimori, *J. Chem. Soc. Japan, Pure Chem. Soc.* (*Nippon Kagaku Zasshi*), **81**, 314 (1960).
9) Y. Urushibara, S. Nishimura and H. Uehara, This Bulletin, **28**, 446 (1955).
10) S. Taira, ibid., **34**, 1072 (1961).
11) K. Hata, K. Watanabe and H. Watanabe, ibid., **32**, 6 (1959).
12) S. Saito, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **76**, 351 (1956).
13) Chem. Soc. Japan, ed., "Jikken Kagaku Kōza", Vol. 17, Part 2, Maruzen, Tokyo (1956), p. 334.

* In the present paper the notation (s) temporarily implies the catalysts obtained from the precipitated metals prepared by the simplified method[1)].

with 100 ml. of ethanol. In this way a grayish black catalyst, contaminated with a small quantity of zinc, was obtained.

b) Urushibara Iron Prepared from Ferrous Chloride, Abbreviated as U-Fe(II).—To a mixture of zinc dust (20 g.) and water (6 ml.) placed in a 50 ml. beaker, the crystal of commercially available ferrous chloride ($FeCl_2 \cdot nH_2O$) containing 2 g. of iron* was added, and then the mixture was warmed on a boiling water bath and stirred with a glass rod for about 2 min. The reaction mixture (precipitated iron) was washed with 300 ml. of cold water, and then the washing was removed by filtration or decantation. The precipitated iron was treated with occasionl stirring in 300 g. of 15% acetic acid at 60～70°C for about 15～20 min. until the generation of hydrogen gas subsided and a solid came up to the surface of the almost colorless solution. The following operation was similar to that described in a). In this way a bulky brownish black catalyst, containing about 2 g. of iron and a considerable quantity of zinc, was obtained.

c) U-Fe(II)-Ni or U-Fe(III)-Ni.—To the mixture of zinc dust (20 or 25 g.) and water (6 or 8 ml.), 0.2 ml. of an aqueous nickel chloride solution (10 ml. of the solution contains 1 g. of nickel) was added, and then the crystal of ferrous or ferric chloride (containing 2 g. of iron) was added. The following procedure was the same as that described in a) or b).

d) U-Fe(II)-Co or U-Fe(III)-Co.—The procedures for the preparation were the same as those for the U-Fe-Ni, but 0.5 ml. of a cobalt chloride solution (10 ml. of the solution contains 1 g. of cobalt) was used.

e) Urushibara Cobalt A Obtained from the Precipitated Cobalt Prepared by a Simplified Method by Treatment with Hydrochloric Acid, Abbreviated as U-Co-A(s)(HCl).—To a mixture of zinc dust (5 g.) and water (1 ml.), 2.02 g. (containing 0.5 g. of cobalt) of the crystal of commercially available cobalt chloride was added, and then the mixture was well stirred with a glass rod. Soon a weak exothermic reaction occurred and the mixture became slushy after about 5 min. The reaction mixture (precipitated cobalt) was washed with 100 ml. of cold water, and then it was treated with 200 ml. of 0.75 N hydrochloric acid at an ordinary temperature. A vigorous reaction took place, and a black solid came up to the surface of the pink solution within one minute. The solid was quickly collected on a glass filter and washed with 200 ml. of cold water and then with 100 ml. of ethanol.

f) U-Co-B(s).—The precipitated cobalt prepared by the simplified method as described in e) was treated with 80 g. of a 10% aqueous sodium hydroxide solution as in the usual way[5,8,13].

In all procedures, purified water was used for washing except for the preparations of precipitated metals. The U-Ni-A(s)(HCl), U-Co-A(s)(HCl) and U-Co-B(s) were prepared thoroughly with city water. The solid should be protected from contact with air as far as possible after the treatment of the precipitated metals with acid or alkali.

Results and Discussion

The Urushibara Iron Catalysts.—The problem of the partial hydrogenation of acetylenic compounds to the corresponding ethylenic compounds has attracted many workers. For the partial catalytic hydrogenation of acetylenic compounds in the liquid phase, it it necessary to stop the hydrogenation when one mole of hydrogen has reacted. Palladium has been accepted as a catalyst whose selective action can be utilized for this partial hydrogenation. Campbell and O'Connor[14] reported that Raney nickel exhibits a similar selective property and used it as a catalyst in the preparation of numerous olefins from the corresponding acetylenes. However, both the palladium and the Raney nickel catalyst are unsatisfactory for the partial hydrogenation because they are excellent catalysts also for the hydrogenation of ethylenic bonds, and the hydrogenation must therefore be watched constantly and stopped at a proper moment so as to prevent the saturation of the ethylenic bonds. Therefore, the publication by paul and Hilly on Raney iron catalyst[15], which has been prepared much like Raney nickel but is unable to effect the hydrogenation of ethylenic linkage, is of considerable importance. It is, however, very troublesome to prepare the iron-aluminum alloy in a laboratory. The procedure of preparing such an iron catalyst would be very simple if the iron particles obtained by the Urushibara method had a similar catalytic activity.

As the difference between the standard electrode potentials of iron and zinc is smaller than the difference between those of nickel, cobalt or copper and zinc, a ferric or ferrous chloride solution can only with difficulty be reduced by zinc dust by the ordinary procedure for preparing precipitated metals. Ferric chloride, however, can react vigorously with zinc dust under conditions similar to that described in the preceding paper[1] as a simplified method for the preparation of precipitated nickel, The precipitated iron thus obtained gives a fine, grayish black solid after treatment with acetic acid. As ferrous chloride reacts gently with zinc dust under the same conditions, external heating is advisable to complete the reaction. The precipitated iron obtained from ferrous chloride gives a fine, brownish

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* As the content of iron in commercially available ferrous chloride is usually indefinite, it should previously be determined by analysis.

[14] K. N. Campbell and M. J. O'Connor, *J. Am. Chem. Soc.*, **61**, 2897 (1939).

[15] P. Paul and G. Hilly, *Bull. soc. chim. France*, [5] **6**, 218 (1939); A. F. Thompson and S. B. Wyatt, *J. Am. Chem. Soc.*, **62**, 2555 (1940).

TABLE. HYDROGENATION OF 2-BUTYNE-1,4-DIOL
2-Butyne-1,4-diol (4.3 g., 0.05 mol.) was dissolved in 50 ml. of ethanol.

Exp. No.	Catalyst	Weight of catalyst, g.[a]	Initial Press. kg./cm^2	Initial temp., °C	Reaction temp., °C	Time[b] min.	Hydrogenation Product
1	U–Fe(III)	2 (2.2)	51	23	23～105[c]	130	*cis*-2-Butene-1,4-diol
2	U–Fe(II)	2 (4.6)	72.5	21	100～105	130	*cis*-2-Butene-1,4-diol
3	U–Fe(III)-BA	2 (1.9)	50.5	28	105～118		None[d]
4[e]	U–Fe(III)	2 (0.65)	56	21	144～154	345	*cis*-2-Butene-1,4-diol
5	U–Fe(III)-Ni	2.02[f](1)	70	21	101～105	60	*cis*-2-Butene-1,4-diol
6	U–Fe(II)-Ni	2.02[f](5.3)	65	24	101～105	70	*cis*-2-Butene-1,4-diol
7	U–Fe(III)-Co	2.05[g](1.6)	78	29	100～103	45	*cis*-2-Butene-1,4-diol
8	U–Fe(II)-Co	2.05[g](5)	62.5	33	100～105	265	*cis*-2-Butene-1,4-diol
9	U–Ni–A(s)(HCl)	0.5 (0.4)	58	24	24～ 36[h]	10	1,4-Butane-diol
10	U–Co–A(s)(HCl)	0.5 (0.6)	60	28	33～ 41[h]	50	*cis*-2-Butene-1,4-diol
11	U–Co–B(s)	0.5 (3)	64	30	31～ 35[h]	70	*cis*-2-Butene-1,4-diol

a) The figures show the net weight of the catalyst metal, which was used as chloride at the beginning of the preparation of the catalyst. The figures shown in the parentheses are the gross weight of dried catalysts after use for hydrogenation.
b) The time required to finish the hydrogenation after hydrogen uptake begins.
c) Agitation was started at room temperature and hydrogen uptake began at about 80°C and the rate increased at about 100°C.
d) Hydrogenation did not get on.
e) 0.1 mol. of the sample in 50 ml. of ethanol was used, and hydrogen gas was charged four times in the course of the operation.
f) Fe 2 g. and Ni 0.02 g.
g) Fe 2 g. and Co 0.05 g.
h) The temperature rose spontaneously by the heat of reaction.

black solid after treatment with acetic acid. Both solids have proved to be active as catalysts. These new catalysts can be named Urushibara iron catalysts, or U–Fe(II) and U–Fe(III) when abbreviated. The figures in parentheses show the original valencies of iron in the chloride. Both U–Fe(II) and U–Fe(III) consist of iron and a quantity of zinc, but the former is somewhat bulkier and contains more zinc than the latter.

In place of zinc dust, aluminum grains are used as a reducing agent for nickel ion in the preparation of the U–Ni–BA[6] or the U–Ni–AA[11]. The diluted ferric chloride solution also reacted vigorously with aluminum grains to give a precipitated iron. However, Urushibara iron BA, similarly obtained by treatment of the precipitated iron with a sodium hydroxide solution, was found to have no catalytic activity.

Partial Hydrogenation of 2-Butyne-1,4-diol.—The partial hydrogenation of 2-butyne-1,4-diol to cis-2-butene-1,4-diol has already been studied by many workers with Raney nickel[16], palladium-calcium carbonate[17], iron[18] or partially poisoned copper, nickel, cobalt and platinum[19] catalysts.

The present author attempted the hydrogenation of 2-butyne-1,4-diol with some Urushibara catalysts and studied the activity of each catalyst. The results are listed in the table. The first experiment was carried out to determine the temperature at which hydrogen uptake begins with the Urushibara iron catalyst. The hydrogen uptake starts at about 80°C, and the rate increased at about 100°C (Exp. No. 1). Accordingly, the following experiments were carried out at about 100°C when the iron catalyst was applied. The result obtained with the U–Fe(II) was similar to that obtained with the U–Fe(III) (Exp. No. 2). No appreciable hydrogen uptake was observed with the U–Fe(III)–BA under similar conditions (Exp. No. 3).

It has been recognized that the increase of the concentration of the substance to be reduced in a solution or the elevation of the reaction temperature exerts a favorable effect on the reduction rate of benzophenone[5].

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[16] A. Valette, *Ann. chim.*, [12] **3**, 667 (1948); C. Prévost and A. Valette, *Compt rend.*, **222**, 327 (1946); N. Lozac'h, *Bull. soc. chim. France*, **1949**, 287; W. Reppe et al., *Ann.*, **596**, 44 (1955); J. Yasumura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 218 (1961).

[17] A. W. Johnson, *J. Chem. Soc.*, **1946**, 1014; T. Fukuda and T. Kusama, This Bulletin, **31**, 339 (1958).

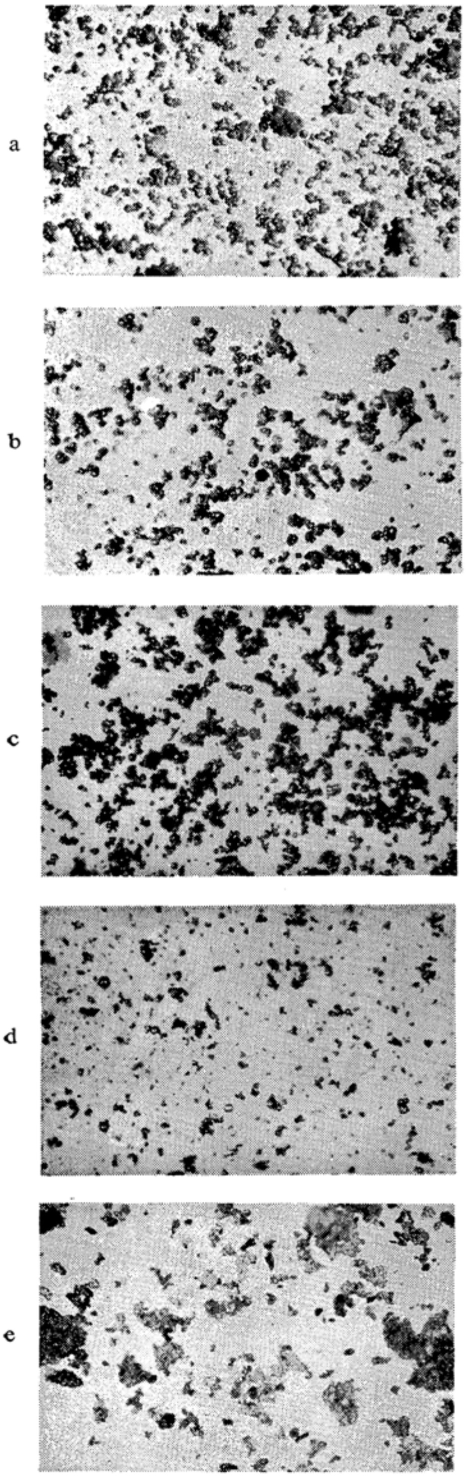
[18] Basf. D. B. P. 873, 545 (1941); *Chem. Zentr.* **1953**, 7401; W. Reppe et al., *Ann.*, **596**, 43, 60 (1955).

[19] I. G. Farbenind., German Pat. 734312 (1938); German Pat. *Org. Chem.*, **6**, 548; General Aniline and Film Corp. U. S. Pat. 2300598 (1939), *Chem. Abstr.*, **37**, 2018 (1943).

Accordingly, the hydrogenation of 2-butyne-1,4-diol was attempted in a concentrated solution at a higher temperature, but the results were unsatisactory (Exp. No. 4), probably because of an insufficiency of catalyst.

As seen from the table, the gross weight of the U–Fe(II) is much more than that of the U–Fe(III), though they are prepared so as to contain the same quantity of iron and are nearly equal in apparent bulk. The U–Fe(II) probably contains more zinc than the U–Fe(III). The micro-photographs of both iron catalysts show that the grains of zinc dust contaminated in them are covered with iron and that many spherical iron-zinc couples coagulate to form a block. The above-mentioned difference between the state of the U–Fe(II) and U–Fe(III) may be supposed to be due to the difference between the nature of the two precipitated irons, because they are treated with acetic acid under nearly identical conditions to give each U–Fe catalyst. Probably the state of iron may differ in the two precipitated irons. The precipitated iron from ferric chloride is found to be more easily eroded by acetic acid during the digestion. Therefore, quick collection of the U–Fe(III) is necessary after the completion of digestion to prepare the catalyst containing a sufficient quantity of iron.

The author found that a U–Ni–A obtained from zinc dust and the precipitated nickel prepared from a nickel chloride solution, contaminated with a little ferric chloride, is more active than the usual U–Ni–A in the reduction of acetophenone. The iron is considered to act as a promoter. It is similarly expected that the addition of a little nickel to the iron may have a favorable effect on the activity of the iron catalyst in the hydrogenation. Actually, such catalysts, U–Fe(II)–Ni and U–Fe(III)–Ni (Fe 1 : Ni 0.01), were proved to have higher activities than the U–Fe(II) or U–Fe(III) (Exp. Nos. 5 and 6). The activity of the iron catalyst may also be increased by the addition of cobalt. As a cobalt catalyst is generally less active than a nickel catalyst in the catalytic reduction, especially in the hydrogenation of carbon-carbon double bonds, the ratio of cobalt to iron in the catalyst may safely be increased in the hydrogenation of carbon-carbon triple bonds. A good result was obtained with the U–Fe(III)–Co (Fe 1 : Co 0.025) (Exp. No. 7). In contrast with the U–Fe(III)–Co, the U–Fe(II)–Co was strikingly low in activity (Exp. No. 8). The cause of this low activity is obscure except for the wrong dispersability of the U–Fe(II) into a solution by the up and down agitation employed in those experiments.



Micro-photographs of Precipitated Irons and Urushibara Iron Catalysts (×75)

(a) Precipitated iron prepared from ferrous chloride. (b) Precipitated iron prepared from ferric chloride (c) U–Fe(II) (d) U–Fe(III) (e) U–Fe(III)–BA

It has been reported in the preceding paper⁽¹⁾ that the U–Ni–A(s) is somewhat lower in activity than the U–Ni–A prepared by the usual method, and that hydrochloric acid can be used for the digestion of the precipitated nickel to give a less active catalyst, U–Ni–A(HCl). Accordingly it is expected that U–Ni–A(s)(HCl) may be much less active than the usual U–Ni–A, and that the partial hydrogenation of the acetylenic bond to the ethylenic bond may safely be attained with the catalyst. However, the catalyst was unexpectedly still so active that butynediol was rapidly hydrogenated to butanediol (Exp. No. 9). It is not yet hopeless with a cobalt catalyst, and the U–Co–A(s)(HCl) and U–Co–B(s) served the purpose, though the hydrogenation should have been checked at the point where the hydrogen uptake became very slow after the absorption of almost stoichiometric hydrogen gas (Exp. Nos. 10 and 11). In these experiments, hydrogen uptake was not obsered for five to fifteen minutes after stirring was started at room temperature. The reaction started when the temperature in the autoclave exceeded about 31°C, and the temperature then went on rising owing to the heat of the reaction. As the room temperature was near 31°C, it was not clear whether the first time lag was due to an induction period or to an inadequate temperature for starting the reaction.

Summary

The Urushibara iron catalysts were newly developed. Partial hydrogenation of 2-butyne-1,4-diol to cis-2-butene-1,4-diol was successfully attained with the iron catalysts, and some modified Urushibara cobalt catalysts were also found to be applicable.

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