Partial Hydrogenation of 1, 4-Butynediol

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For the partial catalytic hydrogenation of acetylenic compounds in the liquid phase, it is necessary to stop the hydrogenation purposely when one molecule of hydrogen has reacted. If we can, however, retard the hydrogenation of ethylenic compounds by some means other than that of acetylenic compounds, the preparation of ethylenic compounds will be simple.

Recently, O. Isler et al.[1] found that the palladium-charcoal catalyst was poisoned by quinoline hydrogenated acetylenic compounds to the corresponding ethylenic compounds, but not to the corresponding saturated compounds. H. Lindler[2] also observed similar phenomena in the hydrogenation of some acetylenic compounds with the palladium calcium-carbonate catalyst poisoned by lead acetate, with the addition of quinoline. W. Oroshnic et al.[3] and B. Elsner et al.[4] found that with the Raney nickel catalyst poisoned by zinc acetate and copper acetate, the hydrogenation of ethylenic compounds was selectively retarded by the addition of piperidine. Since then, some application of these methods have been developed[5].

It was shown that, when the palladium catalyst is poisoned, the hydrogenating activity for acetylenic compounds and that for ethylenic compounds are decreased at different rates[6]. It was also found that, in the case of nitrobenzyl chloride, the hydrogenation takes place selectively when quinoline is added[7]. However, the mechanism of the partial hydrogenation of acetylenic compounds has not clearly been explained.

The present paper describes the experimental results of the hydrogenation of 1, 4-butynediol carried out with the Pd-$CaCO_3$ catalyst poisoned by lead acetate and the poisons, and the partial hydrogenation achieved by using Pd-$CaCO_3$ catalyst with quinoline.

Experimental

Apparatus.—An about 300 cc. usual glass vessel shaken at a constant oscillation was employed.

Materials.—1, 4-Butynediol was recrystallized several times from ethyl acetate. Commercial hydrogen was used. Calcium carbonate was of a commercial extra pure grade (Koso Chemical Co., Tokyo).

Procedures.—Pd-$CaCO_3$ catalyst (Pd-content, 5% by wt.) was prepared from palladium chloride solution according to Lindler[1]. Its poisoning with lead acetate was carried out by adding various amounts of aqueous lead acetate (5g. of $(AcO)_2Pb \cdot 3H_2O$ in 100 cc. of water) to 2 g. of the catalyst. Aqueous 1, 4-butynediol was used. Catalytic hydrogenation was carried out at room temperature (12°～16°C) and at atmospheric pressure, with 250～300 turns oscillation.

Results.—The overall hydrogenation of 1, 4-butynediol proceeded in two distinct steps as shown in Fig. 1. When 30 g. (0.35 mol.) of 1, 4-butynediol in 150 cc. of water was hydrogenated on Pd-$CaCO_3$ catalyst, 8.5 l. (N. T. P.), or 0.38 mol., of hydrogen was absorbed, and the following products were obtained by the distillation of the reaction mixture.

Purified raw material		28 g.
Distillates	i～102°C/3 mmHg	2 g.
	102°～107°C/3 mmHg	19 g.
Decomposed product (found in the trap)		0.7 g.
Residue		5 g.

The product distilling at 102°～107°C/3 mmHg was proved to be a *cis*- and *trans*-1, 4-butenediol mixture by the infrared spectrographic analysis, and found to contain 0.0110 mol. double bond per one gram substance by bromine addition, the theoretical value for pure 1, 4-butenediol being 0.0116 mol.

Fig. 1 shows that the hydrogenation takes place mainly at 1, 4-butynediol in the first step, and then at 1, 4-butenediol. Hydrogenation was carried out with various concentrations of 1, 4-butynediol, 0.3 g. of Pd-$CaCO_3$ being used. The dependency of the initial velocity of the hydrogenation upon the concentration of 1, 4-butynediol is shown in Fig. 2.

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[1] O. Isler. et al.; *Helv. chim. Acta*, **30**, 1911 (1947).

[2] H. Lindler; ibid., **35**, 446 (1952).

[3] W. Oroshnik, G. Karmas and A. D. Mcbane; *J. Am. Chem. Soc.*, **74**, 295 (1952).

[4] B. B. Elsner and P. F. M. Paul; *J. Chem. Soc.*, **1953**, 3156.

[5] a) K. Hofmann and S. M. Sax, *J. Biol. Chem.*, **205**, 55 (1953): see also, L. Luzika and P. Muller, *Helv. chim. Acta*, **22**, 755 (1939); b) J. L. H. Allan, E. R. H. Jones and M. C. Whiting; *J. Chem. Soc.*, **1955**, 1862; c) W. Oroshnic, G. Karmas and A. D. Mcbane, *J. Am. Chem. Soc.*, **74**, 3807 (1952): P. Karrer and J. Kebele, *Helv. chim. Acta*, **35**, 2570 (1952).

[6] K. Tamaru, This Bulletin. **23**, 180 (1950).

[7] K. W. Rosenmond and F. Zetzsche, *Ber.*, **54**, 425 (1921).

The acivation energies of the hydrogenation were calculated to be 2.7 kcal./mol. for 1, 4-butynediol and 5.2 kcal./mol. for 1, 4-butenediol, from the hydrogenation experiments at 0°C and 30°C. The results of poisoning of Pd-$CaCO_3$ catalyst by lead acetate are schematically shown in Fig. 3 and Fig. 4. When 0.3 cc. of pyridine, piperidine, or quinoline was added to the reactant, the hydrogenation proceeded as shown in Fig. 5.

When 30 g. (0.35 mol.) of 1, 4-butynediol in 150 cc. of water was hydrogenated with Pd-$CaCO_3$ catalyst in the presence of 0.3 cc. of quinoline, 8.2 l. (N. T. P.), or 0.37 mol. of hydrogen was absorbed, and then the reaction stopped. From the reaction mixture, the following products were obtained.

Puriefied raw material ....29 g.
Distillates { i~102°C/3 mmHg ...... 1 g.
Distillates { 102°~107°C/3 mmHg ......22 g.
Decomposed product
(found in the trap)..................... 1 g.
Residue.. 5 g.

The product distilling out at 102°~107°C/3 mmHg was proved to be a mixture of *cis*- and *trans*-1, 4-butenediol by the infrared spectrographic analysis, and found to contain 0.0112 mol. double bond per one gram substance by bromine addition.

The Pd-$CaCO_3$ catalyst poisoned by lead acetate was used with 0.3 cc. of pyridine, piperidine or quinoline. The results are schematically shown in Figs. 6~8.

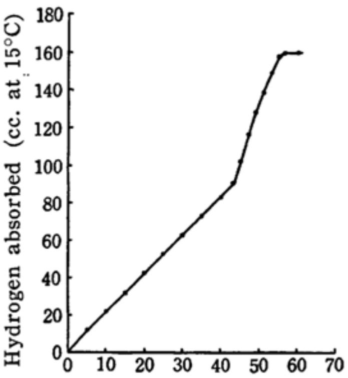

Fig. 1. The hydrogenation rate on Pd-$CaCO_3$ catalyst.

Pd-$CaCO_3$ 0.30 g.
aqueous butynediol 20 cc.
(butynediol, 0.34 g.)
experimental temp. 15°C

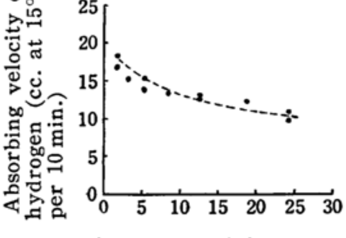

Fig. 2. The effect of the concn. of butynediol on the hydrogenation rate.

Pd-$CaCO_3$ 0.30 g.
aqueous butynediol 20 cc.
experimental temp. 15°C

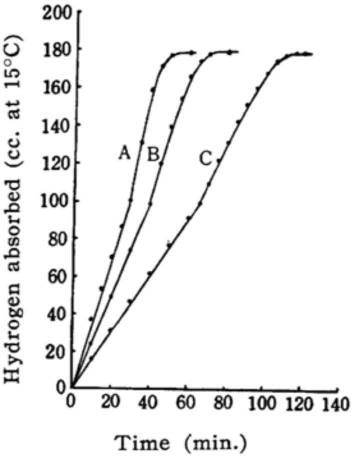

Fig. 3. The effect of lead acetate on the hydrogenating activity of Pd-$CaCO_3$ catalyst.

Pd-$CaCO_3$ poisoned by lead acetate 0.30 g.
aqueous butynediol 20 cc.
(butynediol, 0.34 g.)
experimental temp. 15°C
A: the catalyst poisoned by 0.5 cc. of aqueous lead acetate
B: the catalyst poisoned by 2.0 cc. of aqueous lead acetate
C: the catalyst poisoned by 5.0 cc. of aqueous lead acetate

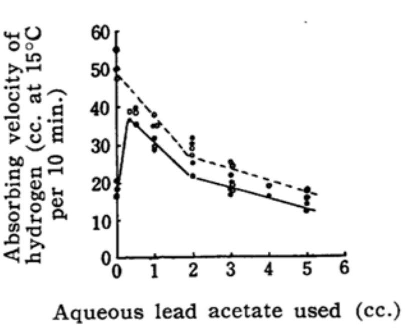

Fig. 4. The effect of lead acetate on the hydrogenating activity of Pd-$CaCO_3$ catalyst.

Pd-$CaCO_3$ poisoned by lead acetate 0.30 g.
aqueous butynediol 20 cc.
(butynediol, 0.34 g.)
experimental temp. 15°C
●: the hydrogenation rate in the 1st step
○: the hydrogenation rate in the 2nd step

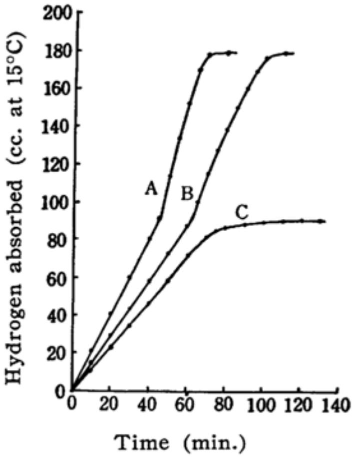

Fig. 5. The effect of poisons on the hydrogenating activity of Pd-CaCO$_3$ catalyst.
Pd-CaCO$_3$ 0.30 g.
aqueous butynediol 20 cc.
(butynediol, 0.34 g.)
experimental temp. 15°C
A: 0.3 cc. of pyridine was added
B: 0.3 cc. of piperidine was added
C: 0.3 cc. of quinoline was added

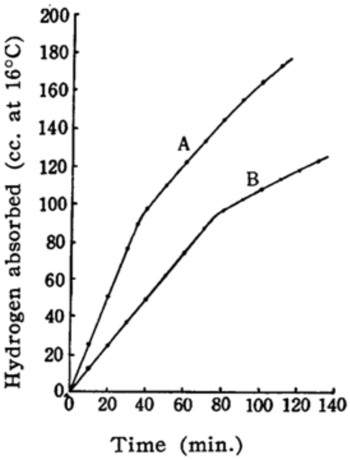

Fig. 6. The effect of pyridine on the hydrogenating activity of the Pd-CaCO$_3$ catalyst poisoned by lead acetate.
Pd-CaCO$_3$ poisoned by lead acetate 0.30 g.
aqueous butynediol 20 cc.
(butynediol, 0.34 g.)
pyridine 0.3 cc.
experimental temp. 16°C
A: the catalyst poisoned by 1.0 cc. of aqueous lead acetate
B: the catalyst poisoned by 5.0 cc. of aqueous lead acetate

Discussion

The hydrogenation of 1,4-butynediol with Pd-CaCO$_3$ catalyst at room temperatures takes place in two distinct steps; the first step is the hydrogenation to 1,4-butenediol, and the second step is its hydrogenation to 1,4-butanediol. The effect of lead acetate and the poisons were

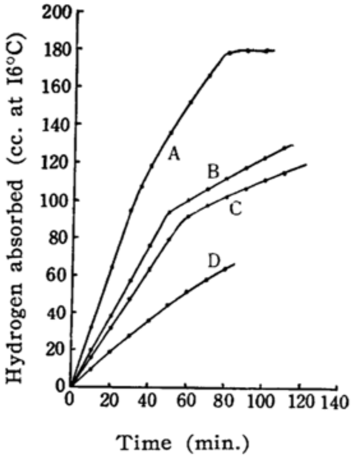

Fig. 7. The effect of piperidine on the hydrogenating activity of the Pd-CaCO$_3$ catalyst poisoned by lead acetate.
Pd-CaCO$_3$ poisoned by lead acetate 0.30 g.
aqueous butynediol 20 cc.
(butynediol, 0.34 g.)
piperidine 0.3 cc.
experimental temp. 16°C
A: the catalyst poisoned by 0.5 cc. of aqueous lead acetate
B: the catalyst poisoned by 0.7 cc. of aqueous lead acetate
C: the catalyst poisoned by 0.9 cc. of aqueous lead acetate
D: the catalyst poisoned by 1.5 cc. of aqueous lead acetate

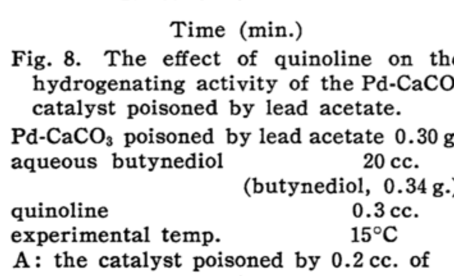

Fig. 8. The effect of quinoline on the hydrogenating activity of the Pd-CaCO$_3$ catalyst poisoned by lead acetate.
Pd-CaCO$_3$ poisoned by lead acetate 0.30 g.
aqueous butynediol 20 cc.
(butynediol, 0.34 g.)
quinoline 0.3 cc.
experimental temp. 15°C
A: the catalyst poisoned by 0.2 cc. of aqueous lead acetate
B: the catalyst poisoned by 0.7 cc. of aqueous lead acetate
C: the catalyst poisoned by 1.0 cc. of aqueous lead acetate

found to be very interesting. When Pd-$CaCO_3$ catalyst is poisoned by increasing amount of lead acetate, the activity for the hydrogenation of 1,4-butynediol increases at first, and then gradually decreases as the poisoning proceeds. On the other hand, that for the hydrogenation of 1,4-butenediol simply decreases with increasing amount of lead acetate. The hydrogenation of 1,4-butynediol is slightly retarded by quinoline, but not by pyridine or piperidine. On the other hand, the hydrogenation of 1,4-butenediol is retarded to some extent by pyridine, more markedly by piperidine and stopped almost completely by quinoline. The effect of these bases is almost the same when they are applied to the Pd-$CaCO_3$ catalyst poisoned by lead acetate. Accordingly, the partial hydrogenation of 1,4-butynediol can be achieved by the use of quinoline.

The reaction velocity in the first step of the hydrogenation is approximated by the following equation, which indicates the retardation of the hydrogenation by 1,4-butynediol,

$$-\frac{\mathrm{d}V}{\mathrm{d}t}=\frac{k}{1+bC}$$

where V denotes the volume of hydrogen absorbed, t, the time, C, the concentration of 1,4-butynediol, and k and b stand for constants. The retardation may result from the strong adsorption of 1,4-butynediol on the catalyst surface. This theory may be supported by the fact that 1,4-butynediol is adsorbed on the catalyst surface prior to 1,4-butenediol, and the latter is unable to be adsorbed while the former is present. Thus, the hydrogenation may take place in two distinct steps.

The phenomena found on the Pd-$CaCO_3$ catalyst poisoned by lead acetate indicate that the properties of the catalyst are changed by the adsorption of lead acetate. It may be stated that, when pyridine, piperidine, or quinoline is added, these substances are adsorbed on the catalyst surface, even when 1,4-butynediol (or lead acetate and 1,4-butynediol) has been adsorbed previously. The properties of the catalyst surface may also be affected by the adsorption of these bases. Their effect on the palladium catalyst might be different from that of lead acetate. Consequently, the selective hydrogenation may take place as observed.

Summary

1. The effect of lead acetate and the poisons on the Pd-$CaCO_3$ catalyst was studied with the hydrogenation of 1,4-butynediol.

2. The hydrogenation of 1,4-butynediol with the Pd-$CaCO_3$ catalyst at room temperatures takes place in two distinct steps; the first step is the hydrogenation to 1,4-butenediol, and the second is its hydrogenation to 1,4-butanediol.

3. When Pd-$CaCO_3$ catalyst is poisoned by increasing amount of lead acetate, the activity for the hydrogenation of 1,4-butynediol increases at first, and then gradually decreases as the poisoning proceeds. On the other hand, that for the hydrogenation of 1,4-butenediol simply decreases with increasing amount of lead acetate.

4. The hydrogenation of 1,4-butynediol with Pd-$CaCO_3$ catalyst is slightly retarded by quinoline, but not by pyridine or piperidine. On the other hand, the hydrogenation of 1,4-butenediol is retarded to some extent by pyridine, more markedly by piperidine, and stopped almost completely by quinoline. The effect of these bases is almost the same when they are applied to the Pd-$CaCO_3$ catalyst poisoned by lead acetate.

5. The partial hydrogenation of 1,4-butynediol can be achieved by using quinoline, but not by using pyridine or piperidine.

6. The selective hydrogenation may result from the strong adsorption of 1,4-butynediol on the catalyst surface. When the catalyst adsorbs the poisons, the properties of the catalyst surface may be changed. As a result, the selectivity of the catalyst may become very characteristic. Consequently, the selective hydrogenation may take place as observed.

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