Competitive Hydrogenation of Acetylenic Compounds

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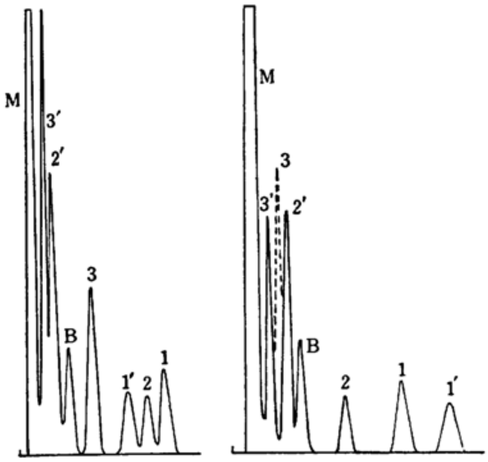
1, 4-Butynediol can be partially hydrogenated on the Pd-$CaCO_3$ catalyst, with quinoline as a poison, and also on the Pd-$BaCO_3$ catalyst poisoned by lead acetate and quinoline, but not on the ordinary palladium catalyst[1,2]. The effect of lead acetate on the Pd-$CaCO_3$ catalyst was different from that of quinoline. It was explained that lead acetate is adsorbed more strongly than 1, 4-butynediol or 1, 4-butenediol, while quinoline is adsorbed in competition with 1, 4-butynediol and 1, 4-butenediol[3].

It seems to be an interesting problem to study in more detail how the properties of the Pd-$CaCO_3$ catalyst are affected by such an additive as quinoline. Thus, the properties of the catalyst for the hydrogenation of phenylacetylene and propargyl alcohol were studied.

Experimental

Procedure. — The hydrogenation experiments were carried out with Pd-$CaCO_3$ catalyst[4] (Pd-content, 5% by wt.), at 25°C and at the atmospheric pressure in methyl alcohol. Phenylacetylene was prepared according to J. C. Hessler[5], and propargyl alcohol was a commercial product[6]. These were purified by distillation. The hydrogenation products were analyzed by gas chromatography.

The gas chromatography experiments were carried out at 100°C by a glass gas chromatography apparatus[7]. Polyethyleneglycol-400 column (P.E.G.-column) and polyethyleneglycol-400-dinonyl phthalate column (P.E.G.-D.N.P-column) were used. With P.E.G.- and P.E.G.-D.N.P.-columns, phenylacetylene, styrene, ethylbenzene, propargyl alcohol, allyl alcohol, and propyl alcohol eluted as shown in Fig. 1.



(A) (B)

Fig. 1. Chromatogram on P.E.G-D.N.P-column and P.E.G.-column, at 100°C.
(A) P.E.G-D.N.P-column : [P.E.G-400-(20%)-celite : D.N.P (20%)-celite =9 : 12 (by wt.)]
length : 2 m., diameter : 4 mm.
(B) P.E.G-column : [P.E.G-400-(20%)-celite] length : 1 m., diameter : 4 mm.
carrier gas : H_2 (50 cc/min.)
1 : Phenylacetylene
2 : Styrene
3 : Ethylbenzene
1' : Propargyl alcohol
2' : Allyl alcohol
3' : Propyl alcohol
B : *n*-Butyl alcohol
M : Methyl alcohol

Results

The hydrogenation of phenylacetylene and propargyl alcohol on the Pd-$CaCO_3$ catalyst took place as shown in Fig. 2. It was shown that phenylacetylene and propargyl alcohol could not be partially hydrogenated in the presence of quinoline.

When 20 millimol. of phenylacetylene or propargyl alcohol in a concentration of 2 millimol./ml. was used, the reaction products were shown in Fig. 3. In these experiments, a mixture of methyl alcohol

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[1] T. Fukuda and T. Kusama, This Bulletin, **31**, 339 (1958).
[2] T. Fukuda, ibid., **31**, 343 (1958).
[3] T. Fukuda, ibid., **32**, 420 (1959).
[4] H. Lindler, *Helv. Chim. Acta*, **30**, 1911 (1947).
[5] J. C. Hessler, "Organic Syntheses", Col. Vol. 1, John Wiley & Sons, Inc., New York, p. 428.
[6] A commercial extra pure grade (Tokyo Kasei Co., Tokyo).
[7] T. Fukuda, *Japan Analyst* (*Bunseki Kagaku*), **8**, 627 (1959).

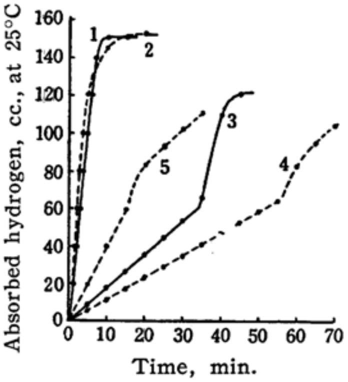

Fig. 2. The absorption of hydrogen in the hydrogenation of phenylacetylene and propargyl alcohol.

Pd-CaO$_3$ catalyst 100 mg.
1: Phenylacetylene (ca. 3.6 millimol.) ···methyl alcohol solution (20 cc.)
2: Phenylacetylene (ca. 3.6 millimol.) ···methyl alcohol-quinoline solution (20 cc.)
3: Propargyl alcohol (ca. 2.8 millimol.) ···aqueous solution (20 cc.)
4: Propargyl alcohol (ca. 2.8 millimol.) ···water-quinoline solution (20 cc.)
5: Propargyl alcohol (ca. 2.8 millimol.) ···quinoline solution (20 cc.)

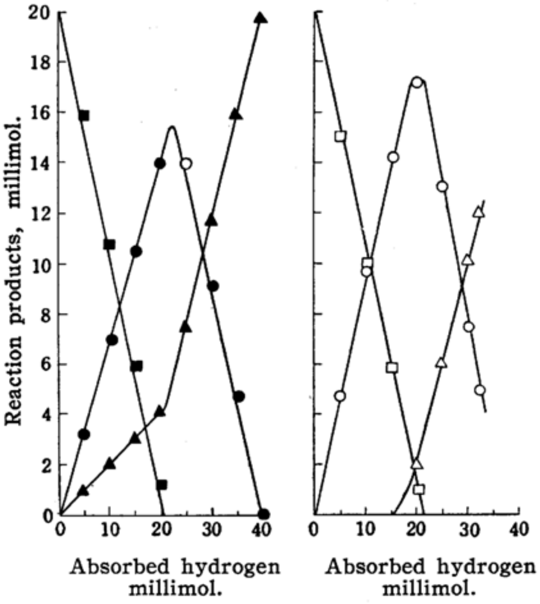

Fig. 3. The reaction products in the hydrogenation of phenylacetylene and propargyl alcohol.

Pd-CaCO$_3$ catalyst 1.00 g.

■ Phenylacetylene	□ Propargyl alcohol
● Styrene	○ Allyl alcohol
▲ Ethylbenzene	△ Propyl alcohol

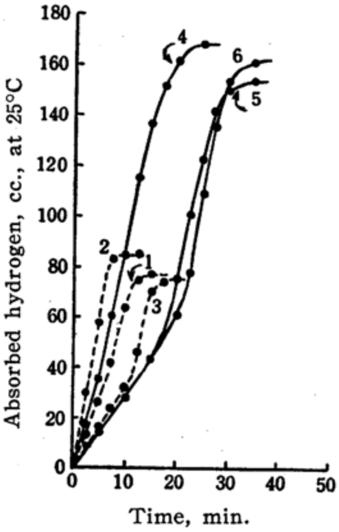

Fig. 4. The absorption rate of hydrogen in the competitive hydrogenation of acetylenic compounds.

Pd-CaCO$_3$ catalyst 100 mg.
Methyl alcohol solution (20 cc.)
1: 1,4-Butynediol (2 millimol.)
2: Phenylacetylene (2 millimol.)
3: Propargyl alcohol (2 millimol.)
4: Phenylacetylene (2 millimol.) +1,4-butynediol (2 millimol.)
5: Propargyl alcohol (2 millimol.) +1,4-butynediol (2 millimol.)
6: Phenylacetylene (2 millimol.) +propargyl alcohol (2 millimol.)

and *n*-butyl alcohol (an internal standard for the gas chromatographic analysis) was used as a solvent. The hydrogenation of phenylacetylene took place with simultaneous hydrogenation of about 20 mol. % of styrene. On the other hand, in the hydrogenation of propargyl alcohol, allyl alcohol was scarcely hydrogenated.

The competitive hydrogenation took place as shown in Fig. 4. When the concentration of the each acetylenic compound was 2 millimol./ml., the reaction products came out as shown in Figs. 5—7, with the absorbed amount of hydrogen. In these experiments, a mixture of methyl alcohol and *n*-butyl alcohol was used as a solvent. The peak of 1,4-butynediol, 1,4-butenediol, and 1,4-butanediol did not appear under the experimental conditions of the gas chromatography. However, the contents of these substances in the product could be roughly estimated from the absorbed amount of hydrogen as shown by the dotted lines, assuming that 1,4-butynediol and 1,4-butenediol were hydrogenated selectively.

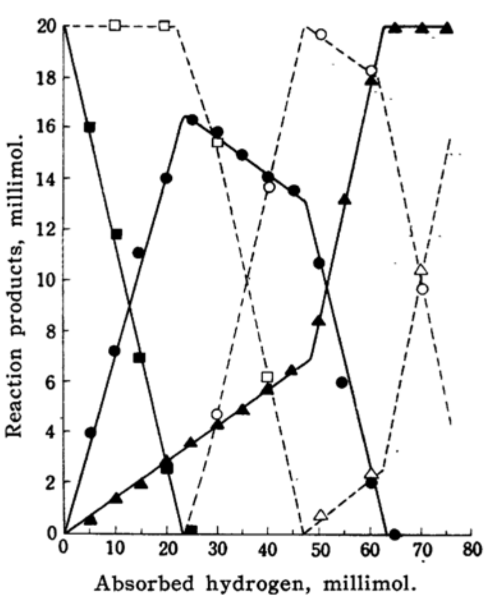

Fig. 5. The reaction products in the competitive hydrogenation of phenylacetylene and 1,4-butynediol.
Pd-$CaCO_3$ catalyst 1.00 g.
Phenylacetylene (20 millimol.)
1,4-Butynediol (20 millimol.)
■ Phenylacetylene □ 1,4-Butynediol
● Styrene ○ 1,4-Butenediol
▲ Ethylbenzene △ 1,4-Butanediol

It was shown that, in the competitive hydrogenation of 1,4-butynediol and phenylacetylene, the latter was hydrogenated first and the former was then hydrogenated, and both steps were accompanied by the hydrogenaion of a small amount of styrene.

The hydrogenation of 1,4-butenediol took place after that of styrene was completed. In the competitive hydrogenation of 1,4-butynediol and propargyl alcohol, the latter was hydrogenated first, and the hydrogenation of 1,4-butynediol with a small amount of allyl alcohol followed. The remaining allyl alcohol was hydrogenated with 1,4-butenediol. In the competitive hydrogenation of phenylacetylene and propargyl alcohol, the latter was hydrogenated with about 35 mol. % of the former. The remaining phenylacetylene was hydrogenated with a small amount of styrene and allyl alcohol. Styrene was hydrogenated with allyl alcohol.

Even when 0.2 millimol./ml. of phenylacetylene (or propargyl alcohol) and 1.8 millimol./ml. of 1,4-butynediol were used, the competitive hydrogenation took place similarly as explained above.

It was observed that an appreciable amount of allyl alcohol was consumed by

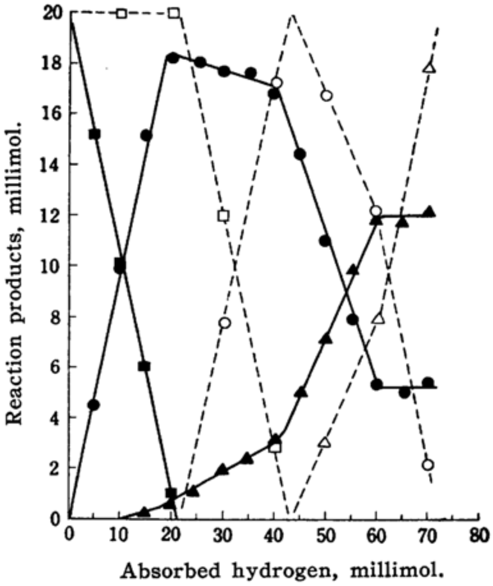

Fig. 6. The reaction products in the competitive hydrogenation propargyl alcohol and 1,4-butynediol.
Pd-$CaCO_3$ catalyst 1.00 g.
Propargyl alcohol (20 millimol.)
1,4-Butynediol (20 millimol.)
■ Propargyl alcohol □ 1,4-Butynediol
● Allyl alcohol ○ 1,4-Butenediol
▲ Propyl alcohol △ 1,4-Butanediol

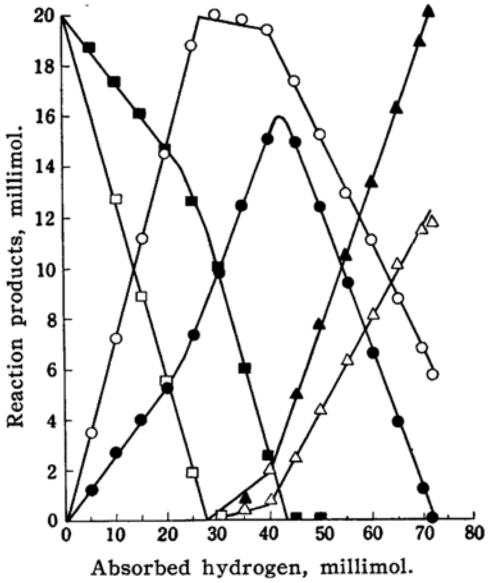

Fig. 7. The reaction products in the competitive hydrogenation of phenylacetylene and propargyl alcohol.
Pd-$CaCO_3$ catalyst 1.00 g.
Phenylacetylene (20 millimol.)
Propargyl alcohol (20 millimol.)
■ Phenylacetylene □ Propargyl alcohol
● Styrene ○ Allyl alcohol
▲ Ethylbenzene △ Propyl alcohol

the side reaction, and its hydrogenation was interrupted with the occurrence of the side reaction. The product from the side reaction was mainly propionaldehyde. However, it was found that propionaldehyde could not retard the hydrogenation of allyl alcohol, a mixture of methyl alcohol and propionaldehyde being used as a solvent.

Consideration

It is interesting to note that, when phenylacetylene has been absorbed on the catalyst surface, styrene is hydrogenated more easily than 1, 4-butynediol, but, when the hydrogenation of phenylacetylene has been completed, 1, 4-butynediol is hydrogenated more easily than styrene. Allyl alcohol is hydrogenated more easily than 1, 4-butenediol. However, 1, 4-butenediol is hydrogenated, even when the hydrogenation of allyl alcohol has been interrupted.

These results show that the catalyst properties are affeced by the adsorption of 1, 4-butynediol, phenylacetylene, propargyl alcohol and so on. It is generally admitted that the catalyst properties are changed by the adsorbed substance[8]. When phenylacetylene or propargyl alcohol is adsorbed on the catalyst surface, the catalyst properties may be different from those when 1, 4-butynediol is adsorbed. Accordingly, the partial hydrogenation of 1, 4-butynediol might have been achieved on the Pd-$CaCO_3$ catalyst, with quinoline as a beneficial poison, but not phenylacetylene and propargyl alcohol.

It was shown that the gas chromatography is very useful to study the reactions.

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