The Poisoning Effect of Lead Acetate and Quinoline

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As previously reported[1], when palladium-calcium carbonate catalyst was poisoned by lead acetate, the activity for the hydrogenation of 1,4-butenediol decreased with increasing amount of lead acetate. It seems likely that, when it is poisoned by a large amount of lead acetate, the activity for the hydrogenation of 1,4-butynediol as well as 1,4-butenediol disappears completely. On the other hand, when palladium-calcium carbonate catalyst was poisoned by quinoline, the activity for the hydrogenation of 1,4-butenediol disappeared almost completely, while that for the hydrogenation of 1,4-butynediol decreased to about a half. Accordingly, it was suggested that the partial hydrogenation of 1,4-butynediol can be achieved by using quinoline as a poison, but not by using lead acetate.

It is a well known fact that the catalyst properties may be changed complicatedly by the adsorption of the poisons[2]. It seems that the properties of palladium-calcium carbonate catalyst are also affected by the adsorption of lead acetate or quinoline. The effect of quinoline might be different from that of lead acetate. Accordingly, the partial hydrogenation of 1,4-butynediol takes place as observed.

However, it seems that the difference in the poisoning effect of lead acetate and quinoline originated also in the difference of the adsorbability between lead acetate and quinoline.

The experiments were carried out by using the aqueous solution of 1,4-butynediol and 1,4-butenediol, at 25°C. The concentration of 1,4-butynediol and 1,4-butene-

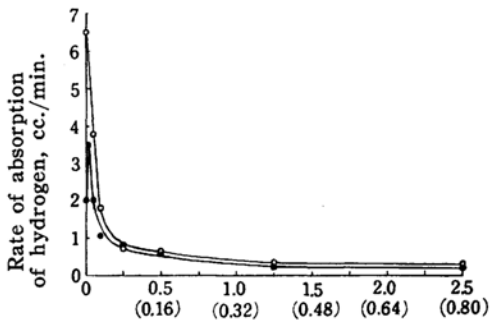

Fig. 1. The poisoning effect of acetate on the hydrogenation of 1,4-butynediol and 1,4-butenediol.
$Pd\text{-}CaCO_3$(5%) 300 mg.
Concentration of 1,4-butynediol (or 1,4-butenediol) 175 μmol./cc.
Oscilaltion 250 turns/min.
● 1,4-butynediol
○ 1,4-butenediol

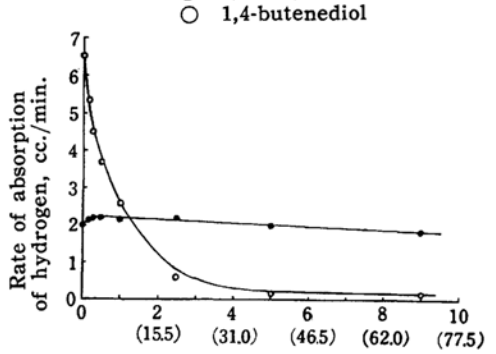

Fig. 2. The poisoning effect of quinoline on the hydrogenation of 1,4-butynediol and 1,4-butenediol.
$Pd\text{-}CaCO_3$(5%) 300 mg.
Concentration of 1,4-butynediol (or 1,4-butenediol) 175 μl./cc.
Oscillation 250 turns/min.
● 1,4-butynediol
○ 1,4-butenediol

1) T. Fukuda and T. Kusama, This Bulletin, 31, 339 (1958).
2) R. Suhrman and K. Schultz, *Z. Phys. Chem. N. F.*, 1, 69 (1954); W. H. Sachtler, *J. Chem. Phys.*, 25, 751 (1956); L. E. Moore and P. W. Selwood, *J. Am. Chem. Soc.*, 78, 697 (1956).

diol was 175 μ mol./cc. The results are shown in Fig. 1 and Fig. 2.

When lead acetate was added to the reactant, the activity of palladium-calcium carbonate catalyst disappeared almost completely with 0.4 μ mol./cc. of lead acetate. When quinoline was used with 0.4 μ mol./cc., the activity for the hydrogenation remained almost unchanged. When it was used 40 μ mol./cc. the activity for the hydrogenation of 1,4-butynediol decreased only a little, but that for the hydrogenation of 1,4-butenediol disappeared almost completely. It is interesting to note that, when the catalyst was poisoned by a small amount of quinoline, the activity for the hydrogenation of 1,4-butynediol increased at first and then decreased with increasing amount of quinoline.

When palladium-calcium carbonate catalyst was poisoned by the larger amount of lead acetate, the activity for the hydrogenation of 1,4-butynediol as well as 1,4-butenediol disappered completely. But, when it was poisoned by quinoline, the activity for the hydrogenation of 1,4-butenediol disappeared completely, while that for the hydrogenation of 1,4-butynediol decreased only a little. These results may explain clearly that lead acetate is adsorbed much more strongly than 1,4-butynediol, but quinoline is not. The catalyst properties are affected by quinoline. Quinoline might be adsorbed competitively with 1,4-butynediol and 1,4-butenediol. As a result, the hydrogenation of 1,4-butenediol is stopped by quinoline, while that of 1,4-butynediol is only retarded.

It may be concluded that the difference in the poisoning effect of lead acetate and quinoline originates also in the difference of the adsorbability between lead acetate and quinoline.

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