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SELECTIVITY OF PALLADIUM AND PLATINUM CATALYSTS IN THE HYDROGENOLYSIS OF 4-HYDROXY- AND 4-METHOXYCYCLOHEXANONES

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Hydrogenolysis of 1,4-cyclohexanedione, 4-hydroxycyclohexanone and 4-methoxycyclohexanone has been studied using palladium and platinum as catalysts. Palladium cleaves the C-O single bond while platinum cleaves the C=O double bond preferentially.

Despite many studies on the catalytic hydrogenolysis of carbon-oxygen bonds,[1,2] little attention has been paid to the mechanism of hydrogenolysis of alicyclic diketones and related compounds. We report here the extent of hydrogenolysis and the selectivity for cleaving the carbon-oxygen single bond against the double bond in the hydrogenation of the bifunctional substrates over platinum group metals.

The reaction of 1,4-cyclohexanedione (I) with hydrogen over palladium and platinum black catalysts was conducted in t-butyl alcohol (0.5 mol/l) at 30°C and atmospheric pressure. 4-Hydroxycyclohexanone (II) and 1,4-cyclohexanediol (III) were produced as the hydrogenation products and cyclohexanone (IV) and cyclohexanol (V) as the hydrogenolysis products. It should be noted that the hydrogenolysis of the carbon-oxygen bond in the alicyclic diketone takes place readily in the neutral medium under mild conditions (see Table 1).

These results prompted us to study the reaction of (II) with hydrogen in comparison with the hydrogenolysis of (I). The main product was (III) on both the metals. Palladium gave (IV) and (V) as the hydrogenolysis products, while platinum gave (V) with a trace of (IV). The formation of (IV) and (V) suggests simultaneous hydrogenolysis of the C-O single bond and the C=O double bond. The mole ratio, (IV)/(V), may be a measure of the selectivity for cleaving the C-O bond vs. the C=O bond. The initial values of the selectivity listed in the Table 1 are quite different between palladium and platinum. The selectivity remained nearly constant during the reaction on platinum, while a decrease was observed on palladium.

(V) may be produced by the direct cleavage of the C=O bond of (II) or by hydrogen addition to (IV) formed by losing the hydroxyl group of (II). In order to make clear this point, we subjected 4-methoxycyclohexanone (VI) to the reaction with hydrogen. The reaction profiles of (VI) were similar to those of (II) on palladium and platinum, respectively. The main product was 4-methoxycyclohexanol (VII) on both the metals. As the hydrogenolysis product, palladium gave (IV) and (V) with a small amount of cyclohexyl methyl ether (VIII) while platinum gave mainly (VIII). The formation of (IV) and (V) on palladium and the formation of

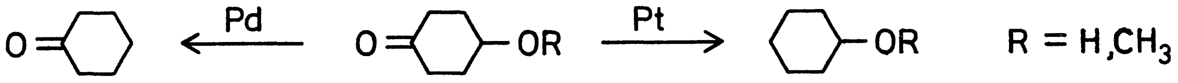
Table 1. Hydrogenolysis of 4-substituted cyclohexanones in t-butyl alcohol at 30°C.

Catalyst	Substrate	Extent of hydrogenolysis (%)[a)]	Selectivity for cleavage[b)]
Pd	1,4-cyclohexanedione	16.3	-
Pt	1,4-cyclohexanedione	50.6	-
Pd	4-hydroxycyclohexanone	7.7	5.9
Pt	4-hydroxycyclohexanone	35.5	0.03
Pd	4-methoxycyclohexanone	3.2	20.4
Pt	4-methoxycyclohexanone	22.5	0.05

[a] Mole percentage of the hydrogenolysis products in all the reaction products at the final stage of the reaction.

[b] Ratio of the cleavage of the C-O bond to that of the C=O bond within 10% of conversion.

(VIII) on platinum indicate that palladium cleaves the C-O bond and platinum cleaves the C=O bond preferentially. In this case, the selectivity for cleavage is unambiguously evaluated by the mole ratio, [(IV)+(V)]/(VIII), and the values at the



initial stage are listed in the Table 1.

No hydrogenolysis of (III), (V), and (VII) occurred over the palladium black under the present condition. This suggests that the cleavage of the C-O bond on the cyclohexyl ring is facilitated with the aid of a carbonyl group on the same molecule.

In support of the direct cleavage mechanism of C=O bond on platinum, the reaction of (VI) with deuterium over the platinum black in t-BuOD gave predominantly the species-d_2 among the deuterated (VIII) at the initial stage of the reaction.

References

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2) A. P. G. Kieboom and F. van Rantivijk, "Hydrogenation and Hydrogenolysis in Synthetic Organic Chemistry," Delft University Press, 1977.

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