Effect of the Particle Size of Catalyst Metal on the Stereochemistry of Hydrogenation

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(Received August 20, 1988)

Synopsis. Particle size of the metal catalysts controlled the stereoselectivity in the hydrogenation of methylenecyclohexanes. No effect of particle size, on the contrary, was observed in the hydrogenation of substituted 3-methylenetetrahydropyran and 5-methylene-1,3-dioxane which contain oxygen atom/atoms in the molecule.

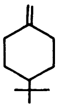
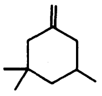
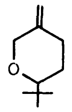
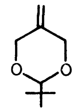
Explanations of the stereochemistry in catalytic hydrogenation have been dominated by ideas concerning the manner in which a given unsaturated compound may best be fitted onto a planar surface from which hydrogen is abstracted; cis addition is the consequences.[1] However, the effect of the steric interaction of substrates with the metallic surface on the product distribution is still complicated.

In order to investigate the correlation between the stereochemistry of hydrogenation and the interaction of the substrate with the catalyst surface, 1-*t*-butyl-4-methylenecyclohexane (**1**), 3,3,5-trimethyl-1-methylenecyclohexane (**2**), 2-*t*-butyl-5-methylenetetrahydropyran (**3**), and 2-*t*-butyl-5-methylene-1,3-dioxane (**4**) were hydrogenated over several transition metal catalysts whose particle sizes of the metal were controlled.

Results and Discussion

The catalysts used in the present study were a Rh and Os colloid in a matrix of poly(*N*-vinylpyrrolidone), and highly dispersed Rh on a SiO_2 surface. Two types of Rh colloid were prepared by the method of Hirai (one type is tentatively named colloid A and the other is colloid B).[2] The average particle diameter of colloid A was reported to be 9 Å and that of colloid B to be 20 Å. The observed particle size of the latter was 27 Å by electron microscope at a magnification of 200000. Two types of Os colloid were similarly prepared as Rh. These Os colloids were highly dispersed and the particle sizes were distributed in very narrow ranges. The average particle diameters of these two types of colloid were 30 Å (colloid A) and 40 Å (colloid B). Three types of Rh supported on SiO_2 were also used as the catalysts. These were 1.0, 4.7, and 14.2% Rh on SiO_2, the average particle sizes of which are 14, 28, and 48 Å, respectively.[3] In some cases, a small amount of endo-cyclic olefins, which were derived by the double bond migration of the original substrates, appeared during the hydrogenation (see Table 1). since the rate of hydrogenation of these endo-cyclic olefins is very slow compared with the original substrates (the apparent rate of hydrogenation of endo-cyclic olefins was less than 1/10 of that of the oiriginal substrates), the appearance of these isomerized olefins with the progress of the reaction seemed to have little influence

Table 1. The Product Distribution of Hydrogenation of Substituted Methylenecyclohexanes, -tetrahydropyran, and -dioxane

Catalyst	Average diameter (Å)	(axial methyl isomer in saturated product (%))			
		 (**1**)	 (**2**)	 (**3**)	 (**4**)
Rh colloid A	9	58(14)[a]	50(9)	96(0)	98(3)
Rh colloid B	27	80(12)	83(6)	97(0)	98(3)
Rh black		90(4)	84(6)	94(0)	98(1)
Os colloid A	30	73(2)	88(1)	97(0)	98(1)
Os colloid B	40	74(2)	93(1)	97(0)	95(1)
Os black		91(2)	89(1)	92(*t*)[b]	92(*t*)
1.0% Rh/SiO_2	14	65(12)	65(7)	94(0)	95(1)
4.7% Rh/SiO_2	28	71(12)	69(8)	95(0)	96(2)
14.2% Rh/SiO_2	48	78(13)	77(10)	95(0)	96(1)

a) Values in parentheses are olefins which are derived by the double bond migration of the original substrates.
b) Trace.

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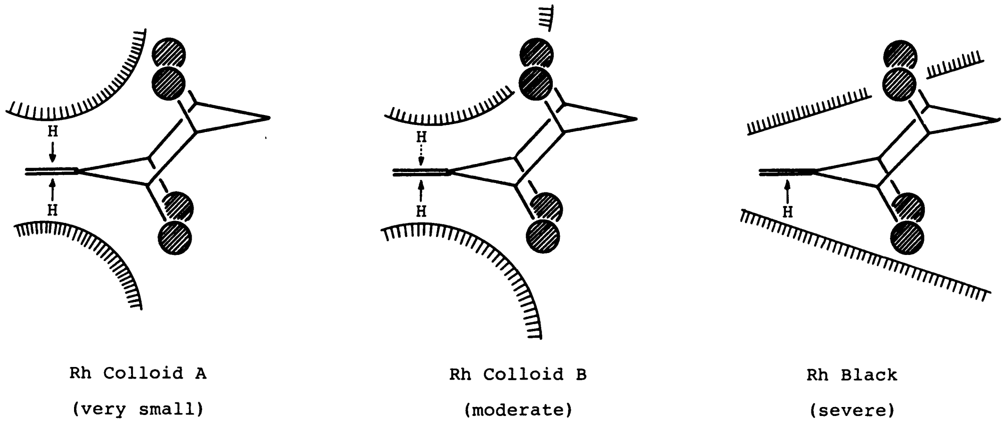
on the epimeric ratios of the saturated products from the original substrates in the early stage of the reaction. The product distribution of the hydrogenation is summarized in Table 1.

The stereochemistry of the hydrogenation of **1** depended on the particle size of the catalyst metal. The ratios of the axial methyl product to the equatorial tend to decrease in the order; black catalyst, colloid B, colloid A on Rh catalyst and those eventually approached unity. A similar trend was observed with Os colloid catalyst. This means that a decrease in the average particle size of the metal colloid gives a decrease in the ratio of the axial methyl isomer. The hydrogenation of **2** also showed the same trend as that of **1**.

Siegel and his co-workers discussed the hydrogenation of cyclic olefins in terms of Horiuti–Polanyi mechanism and proposed that the change in the product-controlling step coincides with a change in the ratio of the products.[4] The distribution of stereoisomeric products will depend upon which of the elementary reactions is product-controlling because the geometry and/or composition of the several possible transition states differ from one another. When the product-controlling step is the adsorption of the substrate on the catalyst or the first hydrogen transfer from the catalyst to the adsorbed species, the stereochemistry of the reaction is controlled by the interaction between the substrate and the catalyst surface.

Since it has been known that the hydrogenation of **1** over noble metal black catalysts always gave cis product,[5] the stereochemistry of the product is considered to be determined by the steric interaction between the substrate and the catalyst surface. Taking into account the average particle size of the catalyst metal together with the product distribution obtained in the present study, the geometries of the adsorption states on the catalyst are illustrated as in Fig. 1, in which the stereochemical correlation of the substrate with the catalyst is imagined. The product distribution leads to the tentative conclusion that (1) the compressional stress of the axial and the equatorial side of a six-membered ring is not very different on the catalyst whose particle size is rather small, so that the attack of hydrogen from either the axial or the equatorial side is roughly equal. This results in the low stereoselectivity of hydrogenation. (2) It is clear from the drawings that the difference of the compressional stress between the axial and the equatorial side increases with increasing particle size of the catalyst metal, so that the adsorption of the substrate becomes easier from the equatorial side than from the axial side. An extremely high axial methyl selectivity is responsible for the overwhelmingly equatorial addition of hydrogen on the metal black catalyst whose particle size of the metal is considered to be macroscopically infinite.

Of particular interest are the results for **3** and **4** which contain the oxygen atom/atoms in the molecule. The compounds containing a polar substituent or atom such as an oxygen or a nitrogen near a reducible double bond are known to exert special directing effect. Presumably, some type of attractive interaction has bound the polar group or atom to the catalyst surface during the hydrogenation so as to enforce the addition of hydrogen from the same side.[6] On the other hand, when the polar atom and the unsaturated group are placed at an appropriate position in the molecule, the directing effect is no longer predominant. For instance, the stereochemistry of the hyrogenation of 2-substituted 5-methylene-1,3-dioxanes over Group VIII transition metal black catalysts made a sharp contrast with that of 4-substituted 1-methylenecyclohexanes. A high cis selectivity was observed in the former, while the latter exhibited a wide variety of diastereomeric product distribution depending on the catalyst metals.[7,8] If the directing effect of the oxygen atom operates, hydrogens should be incorporated from the axial side to give the equatorial methyl isomer. Hydrogen, however, transfers stereoselectively to the unsaturated bond from the opposite side of oxygen lone pairs (Scheme 1). Such high stereoselectivity was interpreted in terms of the presence of the intramolecular interaction between the n orbital of the oxygen atom and the π_{cc} orbital in these compounds.[7,8] In the present study, **3** and **4** gave more than 92% cis product irrespective of the characteristics of the catalysts. This strongly supports that the product distribution of the hydrogenation of these compounds is not controlled

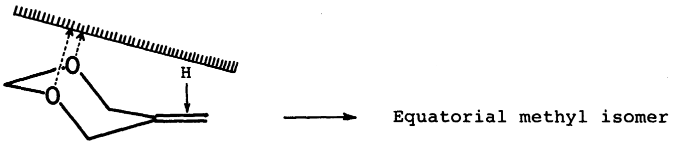


Rh Colloid A
(very small)

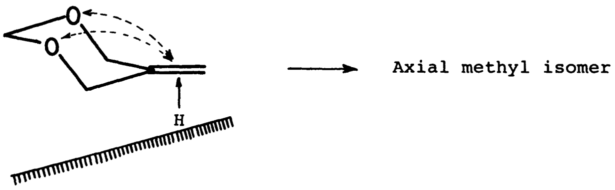
Rh Colloid B
(moderate)

Rh Black
(severe)

Fig. 1. Steric hindrance to adsorption.



Directing effect of oxygen



Intramolecular n_O-π_{CC} interaction

Scheme 1.

by the particle size of the catalyst at all. In other words, the stereochemistry of the hydrogenation seems not to be determined by the steric and/or directing effect, but by the intramolecular orbital interaction.

Experimental

Materials. Compound **3**[8] was prepared by the Wittig reaction[9] of 6-*t*-butyltetrahydropyran-3-one which was obtained by the pyridinium dichromate oxidation of 6-*t*-butyltetrahydropyran-3-ol.[10] Compound **4** has been previously reported.[11]

Catalysts. Rh colloids were prepared by the method of Hirai et al.[2] Os colloid A: OsO_4 (8.5 mg) and poly(*N*-vinylpyrrolidone) (150 mg) were separately dissolved in two portions of methanol (22.5 ml for each). Both solutions were combined and refluxed. After refluxing for 30 min, a methanol solution (5 ml) of sodium hydroxide (6.7 mg) was added dropwise to the solution under reflux, resulting in rapid color change of the solution to dark brown, which corresponded to the formation of Os particles. After further refluxing for 10 min, a dark brown solution of colloid A was obtained. Os Colloid B: OsO_4 (8.5 mg) and poly(*N*-vinylpyrrolidone) (150 mg) were separately dissolved in two portions of ethanol (22.5 ml for each). Both solutions were combined and refluxed. After refluxing for 3 h, a dark brown solution of colloid B was obtained.

Catalytic Hydrogenation. The substrate (0.5 mmol) was stirred in a hydrogen atmosphare in 5 ml methanol (colloid A and black catalysts) or ethanol (colloid B and silica supported catalysts) at room temperature over a weighed catalyst (colloid: substrate/catalyst; 120—250 mol/g-atom, black catalyst: 5 mg, silica supported catalyst: 50 mg). The reaction was followed gas chromatographically by analyzing aliquots of the reaction mixture at appropriate time intervals.

References

1) R. P. Linstead, W. F. Doering, S. B. Davis, P. Levine, and R. R. Whetstone, *J. Am. Chem. Soc.*, **64**, 1985 (1942).

2) H. Hirai, Y. Nakao, and N. Toshima, *Chem. Lett.*, **1978**, 545.

3) H. Arakawa, K. Takeuchi, T. Matsuzaki, and Y. Sugi, *Chem. Lett.*, **1984**, 1607.

4) S. Siegel and B. Dmukovsky, *J. Am. Chem. Soc.*, **84**, 3132 (1962); and the references cited therein.

5) S. Mitsui, K. Gohke, H. Saito, A. Nanbu, and Y. Senda, *Tetrahedron*, **29**, 1525 (1973).

6) M. C. Dart and H. B. Henbest, *J. Chem. Soc.*, **1960**, 3563; C. P. Rader, G. E. Wicks, Jr., R. L. Young, Jr., and H. S. Aaron, *J. Org. Chem.*, **29**, 2252 (1964); T. J. Howard, *Chem. Ind.*, **1963**, 1899; T. J. Howard and B. Morley, *Chem. Ind.*, **1967**, 73; S. Mitsui, Y. Senda, and H. Saito, *Bull. Chem. Soc. Jpn.*, **39**, 694 (1966); S. Mitsui, M. Ito, A. Nanbu, and Y. Senda, *J. Catal.*, **36**, 119 (1975).

7) J-I. Ishiyama, Y. Senda, and S. Imaizumi, *J. Chem. Soc., Perkin Trans. 2*, **1982**, 71; Y. Senda, A. Ohno, J-I. Ishiyama, S. Imaizumi, and S. Kamiyama, *Bull. Chem. Soc. Jpn.*, **60**, 613 (1987).

8) J-I. Ishiyama, S. Kamiyama, Y. Senda, and S. Imaizumi, *Chem. Ind.*, **1988**, 466.

9) R. Greenwald, M. Chaycovsky, and E. J. Corey, *J. Org. Chem.*, **35**, 2654 (1970).

10) C. Anselmi, G. Berti, G. Catelani, L. Lecce, and L. Monti, *Tetrahedron*, **33**, 2271 (1977).

11) E. L. Eliel and N. C. Knoeber, *J. Am. Chem. Soc.*, **92**, 3444 (1970).