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STEREOSELECTIVITY PATTERNS OF THE PLATINUM METALS IN THE CATALYTIC HYDROGENATION OF SOME CYCLOOLEFINIC COMPOUNDS

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The stereoselectivity of the platinum metals in the catalytic hydrogenation of 1,2- and 1,6-dimethylcyclohexene, 1-methyl-2-methylenecyclohexane and 6-ethoxy-1-methylcyclohexene has been studied. The formation of trans isomer increased in the order Ir < Os < Pt,Ru,Rh << Pd. This order in stereoselectivity has been related to the olefin isomerization activities of the metals.

The stereochemistry of the hydrogenation of cycloolefins over platinum metals has been the subject of considerable interest in recent years.[1)] However, comparative studies on it with the six platinum metals are rather few and, in particular, the stereochemical nature of osmium and iridium metals in the hydrogenation is little known.

In a previous communication,[2)] we have shown that over osmium and iridium catalysts 1,2-dimethylcyclohexene (I) and o-xylene are hydrogenated with high stereoselectivity to cis-1,2-dimethylcyclohexane at 25°C and atmospheric hydrogen pressure. Subsequently, the comparative study of the platinum metals including these metals has been extended to the hydrogenation of 1,6-dimethylcyclohexene (II), 1-methyl-2-methylenecyclohexane (III) and 6-ethoxy-1-methylcyclohexene (IV), and it has been found that the order in stereoselectivity of the platinum metals in the hydrogenation of these compounds may be understood roughly as a function of their activities to isomerize the olefins during hydrogenation.

Table 1 presents the proportions of trans isomer formed in the hydrogenation of I, II, III and IV, along with the proportions of isomerization at the initial stages of the hydrogenation of II and III. All the compounds listed in Table 1 give the

Table 1. Proportions of trans Isomer and of Isomerized Product in the Hydrogenation of Cycloolefinic Compounds (%)[a]

Catalyst	Proportion of trans isomer in saturates from hydrogenation of					Proportion of isomerized product[d] in hydrogenation of	
	I	II	III	IV		II[e]	III[f]
				A[b]	B[c]		
Ru	6.5	13.1	34.5	8.8	14.6	2.6	2.0
Rh	12.4	21.5	36.2	10.3[g]	14.0	2.7	2.6
Pd	73.6	71.1	69.2	28.8[g]	23.5[g]	44.1	69.0
Os	1.3	13.0	15.6	1.9	6.2	1.1	0.1
Ir	0.8	11.0	14.6	0.14	2.1	0.8	0.0
Pt	20.9	19.4	34.5	11.3[g]	9.2	2.5	0.27

a) Unless otherwise noted, the substrate (0.1-0.15 ml) was hydrogenated in 4-5 ml of t-BuOH at 26°C and atmospheric pressure. I: 1,2-dimethylcyclohexene; II: 1,6-dimethylcyclohexene; III: 1-methyl-2-methylenecyclohexane; IV: 6-ethoxy-1-methylcyclohexene. b) Solvent, EtOH. c) Solvent, t-BuOH. d) The values were obtained at initial stages of the hydrogenation. e) Given by 100 x mol(I)/mol(II converted). f) Given by 100 x mol(I + II)/mol(III converted). g) The hydrogenation was accompanied by rather extensive hydrogenolysis to give methylcyclohexane (29% on Rh in EtOH, 63% on Pd in EtOH, 54% on Pd in t-BuOH, and 15% on Pt in EtOH).

cis isomer in excess on hydrogenation except in the cases of I, II and III with palladium where the trans isomer is formed predominantly in accord with the results by Siegel and Smith.[3] It is noteworthy that osmium and iridium which afford only slight amounts of trans isomer in the hydrogenation of I are also the metals that give the smallest amounts of trans isomer in the hydrogenation of II, III and IV. On the other hand, palladium gave the largest amounts of trans isomer among the platinum metals in all compounds investigated. Platinum, ruthenium and rhodium are always between the extreme metals mentioned above in their stereoselectivity. Thus, the order in stereoselectivity of the platinum metals is given by Ir < Os < Pt,Ru,Rh << Pd in increasing tendency for formation of trans isomer, irrespective of the compounds hydrogenated.

The extent of isomerization to I in the hydrogenation of II increases in the order Ir < Os < Pt ≤ Ru ≤ Rh << Pd. The same order was also obtained in the isomerization of III to I and II (see Table 1). It is of interest that isomerization of III always occurs more to II than to I which can be easily observed at initial stages of the hydrogenation.

If we plot the trans/cis isomer ratios obtained in the hydrogenation of I, II,

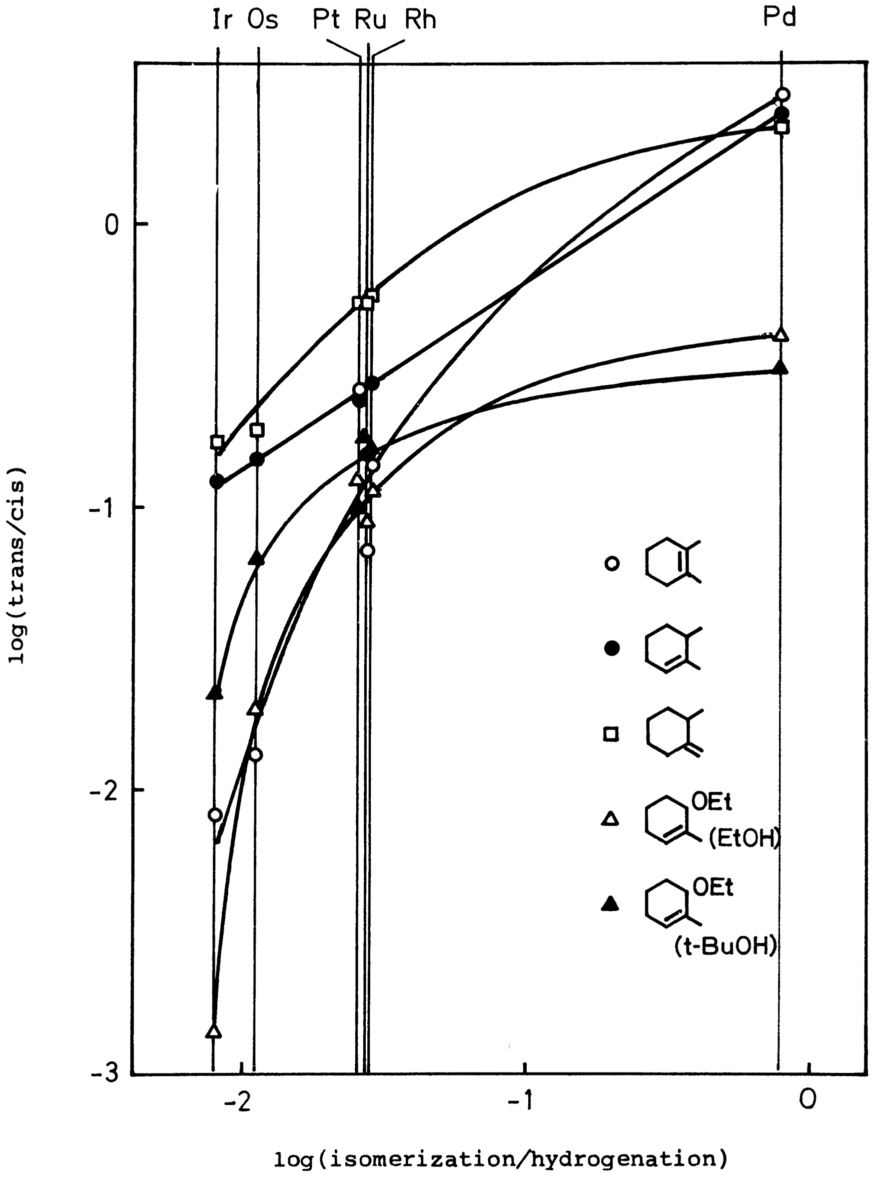

Fig. 1. Stereoselectivity patterns of the platinum metals in the hydrogenation of cycloolefinic compounds; plot of log(trans/cis ratio) against log of the isomerization to hydrogenation ratio in 1,6-dimethylcyclohexene.

III and IV against the isomerization to hydrogenation ratios obtained in the hydrogenation of II, as shown in Fig. 1 in their logarithms, it is clearly seen that the stereoselectivity of the platinum metals is roughly a function of their olefin isomerization ability in any of the compounds investigated.4) The results obtained here may give a support for the mechanism proposed by Siegel and Smith5) to explain the formation of trans isomer in the hydrogenation of I over platinum. According to their mechanism the formation of trans isomer should arize through isomerization of I to II and III followed by desorption from the catalyst surface. It is not certain, however, whether the mechanism can explain the formation of trans isomer quantitatively, since the detectable amounts of isomerized olefins are very small in the hydrogenation of I.

Formation of cis isomer in high yields in II, III and IV over the metals of low isomerization activity suggests that the substituents at allylic position can direct to give more cis isomer on adsorption of the compounds to the catalyst surface. This is consistent with the fact that the substituent at an allylic position in cyclohexenes is likely to be in quasi-axial or axial (in III) conformation.6,7) However, an extremely high stereoselectivity as observed in the hydrogenation of IV over iridium in ethanol (cis: trans = 713: 1) seems difficult to explain by the steric requirment of the ethoxyl group alone.8) It is also noted that cis isomer is produced in higher yields in ethanol than in t-butyl alcohol over osmium and iridium,while the situation was reversed in the hydrogenation of II over the same metals.9)

The catalysts used in this study are unsupported metals which were prepared by the methods descibed previously.10)

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