CHEMISTRY LETTERS, pp. 1625 - 1628, 1984.

SELECTIVITIES OF THE PLATINUM GROUP METALS IN DEUTERATION OF 1,2- AND 1,6-DIMETHYLCYCLOHEXENES

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The deuteration of 1,2- and 1,6-dimethylcyclohexenes over the six unsupported platinum metals has been studied at 25 °C and atmospheric pressure. The stereoselectivities and the degrees of exchange in the formation of saturates have been found to be correlated.

The stereochemistry of the hydrogenation of cycloolefins over the transition metals has been the subject of considerable interest, particularly in relation to the hydrogenation mechanism.1) The reaction of deuterium with cycloolefins may give further information on the interpretation of the stereoselectivities of catalyst metals.2-4)

In a previous paper5) we have shown that the stereoselectivities of the platinum group metals are related to their olefin isomerization activities in the hydrogenation of 1,2- and 1,6-disubstituted cyclohexenes and 1-methyl-2-methylenecyclohexane. Subsequently we have deuterated 1,2- and 1,6-dimethylcyclohexenes and have found that the stereoselectivities of the platinum metals are related to the degrees of exchange accompanying the deuteration in the resulting saturated products. The deuteration has been performed in cyclohexane at 25 °C and atmospheric pressure with the six unsupported platinum metals as catalysts. The catalysts used were prepared by hydrogen reduction of the corresponding metal oxides or hydroxides in water suspensions. Care was taken to remove trace amounts of alkaline and/or acidic impurities by repeated reductions and washings.6,7)

Table 1 shows the isotopic distributions of the products from hydrogenation of 1,2-dimethylcyclohexene obtained by a mass spectral analysis. In agreement with the previous results which were obtained in t-butyl alcohol as a solvent,5) the cis/trans isomer ratios of the 1,2-dimethylcyclohexane formed increased in the order: Pd << Pt < Ru $\simeq$ Rh < Os < Ir. The degrees of exchange as expressed by average deuterium numbers in the saturates, d_{av}'s given by (d_{av}(cis)x mol fraction of cis + d_{av}(trans)x mol fraction of trans), also increased in the same order, as clearly seen in Fig. 1. In general the d_{av}'s and cis/trans isomer ratios increase with increasing conversion, but the variations are not significant and the relationship as shown in Fig. 1 holds for wide range of conversion. The low value of d_{av} for palladium is more pronounced at a lower conversion to saturates (d_{av}: 1.49 at 21.3% conversion compared to 2.12 at 54.8% conversion)(see footnote d), Table 1). In this case a high degree of dilution of the surface deuterium appears to have been caused by rapid isomerization to 1,2- to 1,6-dimethylcyclohexene, since the

Table 1. Isotopic Distribution (d_i in %) of the Products in Deuteration of 1,2-Dimethylcyclohexene[a,b)]

	Catalyst																		
	Ru			Rh			Pd[d)]				Os			Ir			Pt[f)]		
Compd.[c)]	1,2	cis	trans	1,2	cis	trans	1,2	1,6	cis	trans	1,2	cis	trans	1,2	cis	trans[e)]	1,2	cis	trans
(mol%) / d_i	(52.1)	(44.1)	(3.8)	(60.1)	(36.9)	(3.1)	(37.6)	(7.6)	(16.1)	(38.7)	(50.0)	(49.4)	(0.64)	(58.6)	(41.1)	(0.27)	(75.2)	(16.4)	(8.4)
d_0	80.0	10.5	5.9	81.9	11.9	14.4	55.7	17.8	24.5	24.4	93.2	4.0	5.4	91.2	0.5		90.4	7.5	12.7
d_1	10.7	21.3	12.6	6.5	19.9	21.4	18.6	20.7	23.7	24.8	3.7	12.2	7.6	4.7	3.1		6.5	23.9	28.9
d_2	4.7	20.7	19.2	3.6	18.1	18.6	12.8	19.0	19.2	16.5	1.3	23.1	12.4	1.5	12.9		1.5	31.8	26.0
d_3	1.9	17.4	18.5	2.4	16.0	15.5	7.3	19.1	10.7	13.0	0.8	13.3	15.3	0.9	23.9		0.7	20.2	17.4
d_4	0.9	11.3	14.8	1.8	11.1	11.5	2.7	13.0	7.7	8.7	0.5	12.9	14.7	0.8	17.5		0.4	7.3	7.6
d_5	0.7	8.3	11.0	1.2	7.7	6.9	1.5	5.5	6.7	6.0	0.5	12.2	12.8	0.5	15.2		0.4	3.9	4.1
d_6	0.5	4.6	7.6	1.2	5.4	4.6	0.7	2.7	3.4	2.6		8.1	9.8	0.4	9.8			2.6	1.4
d_7	0.5	2.4	4.3	0.9	4.0	3.0	0.5	1.3	1.7	1.7		4.4	7.9		4.8			1.3	0.9
d_8	0.2	1.3	2.6	0.6	2.6	1.7	0.2	0.5	0.9	0.9		3.1	4.7		3.7			0.7	0.5
d_9		1.0	1.5		1.4	1.1		0.4	0.6	0.5		2.7	4.0		2.9			0.3	0.3
d_{10}		0.6	0.7		1.1	0.8			0.4	0.4		1.7	2.3		1.6			0.2	0.2
d_{11}		0.4	0.7		0.5	0.5			0.3	0.3		1.3	1.3		1.5			0.2	
d_{12}		0.2	0.3		0.4				0.2	0.3		0.8	0.9		1.1			0.1	
d_{13}			0.3									0.3	0.9		0.7				
d_{14}															0.5				
d_{15}															0.3				
d_{av}	0.41	2.78	3.53	0.52	3.02	2.71	0.94	2.28	2.13	2.12	0.13	3.84	4.49	0.19	4.61		0.15	2.35	2.07

a) 1,2-Dimethylcyclohexene (50 μl) was deuterated in cyclohexane (2 ml) at 25°C and atmospheric pressure over unsupported metals (2-7 mg). b) d_i: % of the species containing i deterium atoms; d_{av}: average number of deuterium atoms per molecule. c) 1,2: 1,2-dimethylcyclohexene unsaturated; 1,6: 1,6-dimethylcyclohexene formed by isomerization; cis: cis-1,2-dimethylcyclohexane; trans: trans-1,2-dimethylcyclohexane. d) d_{av}'s for cis and trans isomers were 1.63 and 1.44, respectively, at 21.3% conversion to the saturates with cis/trans isomer ratio of 0.385. e) The amount of the trans isomer was too small for precise analysis. d_{av} at complete conversion was 6.30, compared to 5.10 for the cis isomer. f) d_{av}'s at 73.7% conversion were 2.38 and 2.19 for the cis and trans isomers, respectively.

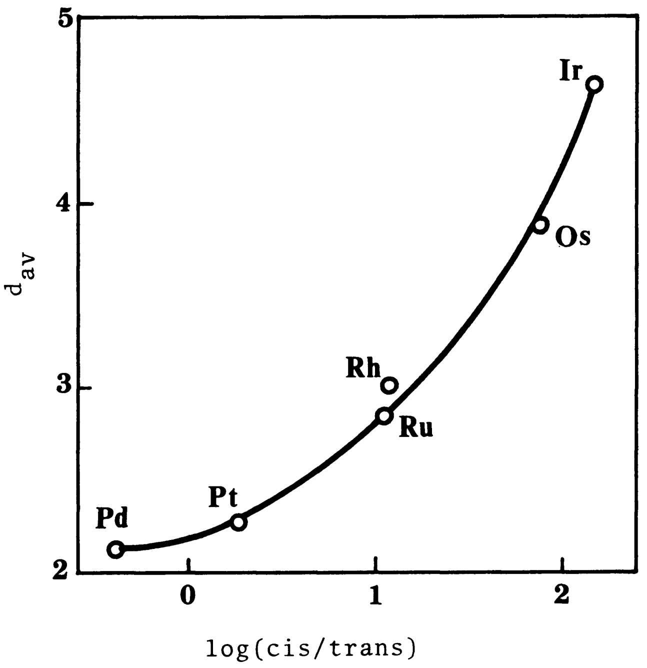

Fig. 1. Deuteration of 1,2-dimethylcyclohexene: relationship between d_{av}'s and cis/trans isomer ratios in saturated products.

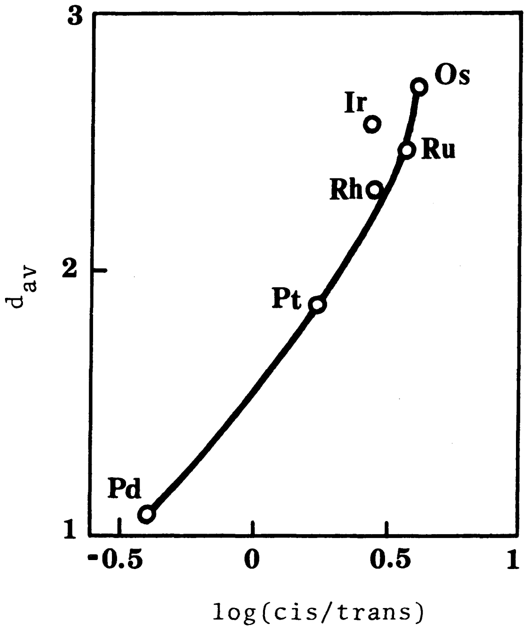

Fig. 2. Deuteration of 1,6-dimethylcyclohexene: relationship between d_{av}'s and cis/trans isomer ratios in saturated products.

Table 2. Average Deuterium Numbers (d_{av}) of the Products in Deuteration of 1,6-Dimethylcyclohexene[a)]

Catalyst	Composition of reac. mixture /mol%				Isomerization	d_{av}			
	1,6	1,2	cis	trans	to 1,2 [b)]/%	1,6	1,2	cis	trans
Ru	62.90	1.19	28.26	7.65	3.21	0.40	-	2.46	2.55
Rh	66.23	1.10	24.01	8.66	3.26	0.19	-	2.44	2.02
Pd	38.93	28.79	9.19	23.09	47.1	0.44	0.72	1.24	1.02
Os	73.96	0.09	20.85	5.10	0.35	0.13	-	2.77	2.45
Ir	73.88	0.10	19.06	6.96	0.38	0.12	-	2.64	2.39
Pt	74.48	0.74	15.66	9.12	2.90	0.10	1.22	1.91	1.80

a) For the reaction conditions and the notations of the compounds, see the footnotes in Table 1. b) Given 100 x mol (1,2)/mol (1,6 converted).

isomerized product is highly exchanged (see Table 1). Although d_{av} for platinum is given at a lower conversion than for the other metals, the value increased only slightly from 2.26 at 24.8% conversion to 2.32 at 73.7% conversion (see footnote f), Table 1).

Table 2 shows the results on the deuteration of 1,6-dimethylcyclohexene. A similar relationship between d_{av}'s and cis/trans isomer ratios in the saturates is also obtained, as shown in Fig. 2, although iridium deviates from the curve. Since previously iridium gave the highest cis/trans isomer ratio with the 1,6 isomer in t-butyl alcohol, as with the 1,2 isomer,5) iridium appears to be located in a rather undue position with respect to its stereoselectivity in Fig. 2. The order in the isomerization of 1,6- to 1,2-dimethylcyclohexene during deuteration is: Pd >> Rh $\geq$ Ru $\geq$ Pt >> Ir $\geq$ Os (see Table 2) and in good agreement with the previous results.5) It is, however, noted that platinum gave a lesser amount of the isomerized product than ruthenium and rhodium, whereas the stereoselectivitiy is considerably lower over platinum than over ruthenium and rhodium. The situation is also similar in deuteration of 1,2-dimethylcyclohexene (see Fig. 1).

Both with 1,2- and 1,6-dimethylcyclohexenes the degrees of exchange in the remaining olefins are the greatest with palladium and the smallest with the 3rd row metals (Os, Ir, Pt)(Tables 1 and 2). The results are generally consistent with the trends of the platinum metals in olefin isomerization given above, although the values for platinum appear too small compared to the extent of isomerization on it. As would be expected, the degrees of exchange are always much higher in isomerized olefins than in remaining starting olefins.

The results described here clearly indicate that the stereoselectivities of the platinum metals are closely related to their d_{av}'s for the saturated products obtained in deuteration of 1,2- and 1,6-dimethylcyclohexenes. Since the stereoselectivities increase with decreasing olefin isomerization activities of the metals as here and previously5) shown, it results that the d_{av}'s increase also with decreasing olefin isomerization activities of the metals. The formation of highly deuterated saturates over osmium and iridium indicates that the surface hydrogen can easily be exchanged with the vapor phase deuterium during deuteration and suggests a weak adsorption of hydrogen over these metals.8) In contrast, with palladium and platinum the surface deuterium which has been diluted with hydrogen appears to be consumed without being enriched by the vapor phase deuterium.2,8) The difficult exchange of the surface hydrogen with palladium and platinum suggests that hydrogen is rather strongly adsorbed over these metals, although olefins appear to be adsorbed rather weakly over palladium as presumed from the extensive isomerization occurring on this metal. It might be possible that the natures of the platinum metals towards hydrogen adsorption have some relations with their olefin isomerization activities and hence their stereoselectivities. In this connection it will be of interest to note that both palladium and platinum can catalyze the acetal formation efficiently in the hydrogenation of cyclohexanones and their enol ethers in ethanol, while osmium and iridium catalyze it only moderately. The acetal formation is catalyzed in the presence of adsorbed hydrogen, probably in an ionized state.6,9)

References

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(Received June 7, 1984)