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# 90. Haruhiko Yamamoto, Kunio Noda, Hiroyuki Horiguti, and Takao Kwan : Stereoselective Hydrogenation of *o*-, *m*-, and *p*-Xylenes by Transition Metal Catalysts of Group Ⅷ.

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The stereoselective hydrogenation of three xylene isomers to yield *cis*- and *trans*-dimethylcyclohexane has been investigated on eight kinds of transition metal catalysts by the gas chromatographic pulse technique. The selectivity for the formation of *trans*-dimethylcyclohexane was found to be of the following sequence with respect to the hydrogenation of *o*-, *m*- and *p*-xylene.

Pd>Co>Ni>Pt>Rh>Ir>Ru ...... *o*-xylene
Rh>Pt～Ru>Co～Ni>Ir .......... *m*-xylene
Co>Pd>Ni>Pt>Rh>Ir>Ru ...... *p*-xylene

It was pointed out that the selectivity sequence parallels with the ability of the transition metals to form $\pi$-allylic complexes in the case of the hydrogenation of *o*- and *p*-xylene and that the remarkable suppression of transformation, as found in the case of *m*-xylene, is due to the steric hindrance rather than the poor ability of the transition metals to form an adsorbed $\pi$-allylic adsorbed intermediate on the surface.

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Transition metals of group Ⅷ have been used widely as the hydrogenation catalysts and it may now be considered that the relative catalytic activity of these metals has been nearly known at least for the hydrogenation of simple olefins. Less information is available, however, concerning the stereoselective hydrogenation of aromatics by the transition metal catalysts. It is the purpose of the present paper to investigate how *cis* and *trans* isomers are produced during the hydrogenation of *o*-, *m*- and *p*-xylenes by the transition metals of group Ⅷ.

Transition metals investigated here as the catalysts were iron, cobalt, nickel, ruthenium, rhodium, palladium, iridium and platinum.

Special interest was laid, first, on these metals for the formation of *trans* isomer and, second, on the difference, if any, in the stereoselectivity of hydrogenation of three xylene isomers by a given metal. It will be suggested in the forthcoming paper[1] that the catalytic hydrogenation of xylene to yield *trans*-dimethylcyclohexane may partly be associated with a $\pi$-allylic intermediate formed on the surface during the hydrogenation. Such a correlation will further be investigated in the present paper.

## Experimental

Basic carbonates of nickel, cobalt and iron were prepared from their nitrates in the usual manner. In the case of ruthenium, rhodium, palladium, iron and platinum, they were impregnated from their chloride solution on silicon carbide which was supplied by Fujimi Kenma Inc. The Brunauer-Emmett-Teller surface area of the support was less than 1 m²/g. About 1 g. on the transition metal catalyst with or without support was respectively packed in a stainless steel reaction tube. The tube was then connected to the separation column of a gas chromatograph.

The reduction of the catalyst was carried out at 350° for several hours in a stream of hydrogen. In the case of iron, it was performed at 450° for about 50 hours.

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[1] H. Yamamoto, H. Horiguti, K. Noda, T. Kwan : This Bulletin, to be published soon.

The apparatus and procedure for the measurements of the hydrogenation of three xylenes were quite the same with those reported previously.1,2) Shimadzu gas chromatograph of the type GC-1B was modified in order to bear upon the pulse technique which was again utilized for the purpose of the present paper.

## Results

The ratio of *cis*-dimethylcyclohexane to *trans*-dimethylcyclohexane produced during the hydrogenation of xylenes will be taken as a measure of the stereoselectivity shown by the respective metal catalyst. Preliminary experiments showed that the ratio is little dependent on such parameters as sample size, contact time, catalyst activity and the kind of support, but definitely dependent on the kind of transition metal used as the catalyst. Thus, the ratio was primarily investigated on each metal against temperatures ranging from 140 to 240° with respect to three isomeric xylenes.

The results are shown in Fig. 1, 2 and 3 respectively.

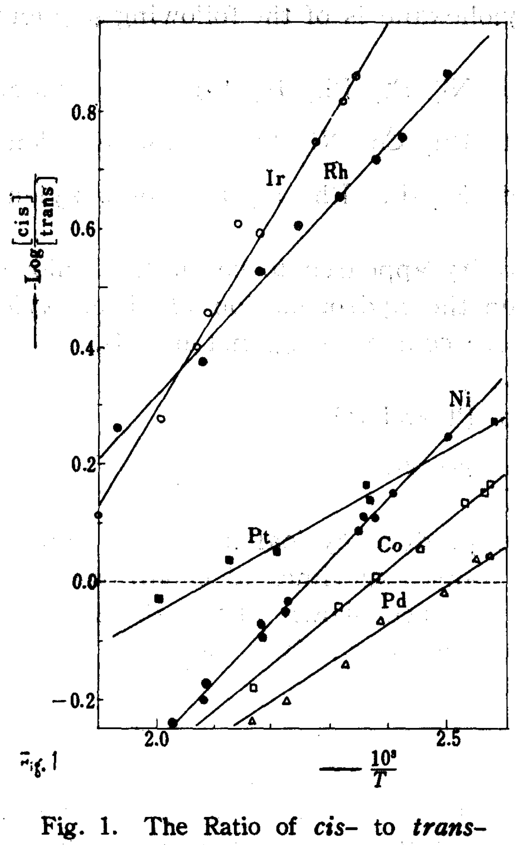

Fig. 1. The Ratio of *cis*- to *trans*-dimethylcyclohexane formed by the Hydrogenation of *o*-Xylene on Transition Metal Catalysts

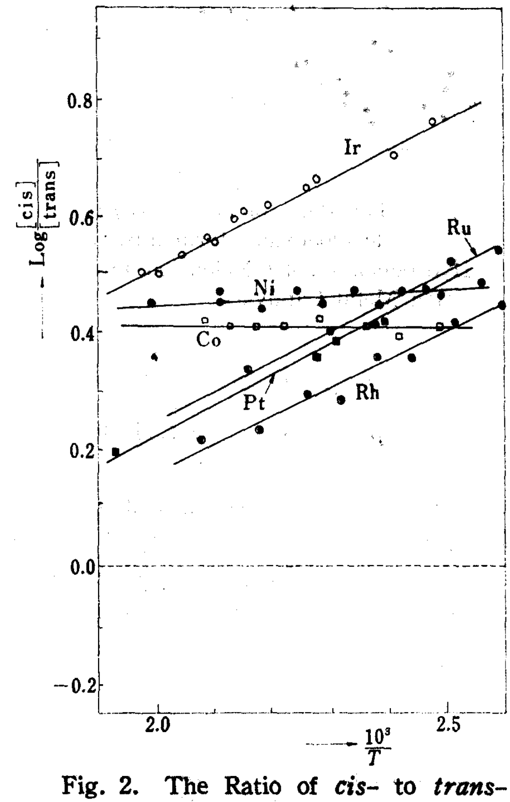

Fig. 2. The Ratio of *cis*- to *trans*-dimethylcyclohexane formed by the Hydrogenation of *m*-Xylene on Transition Metal Catalysts

Iron revealed almost no appreciable activity for the hydrogenation of xylenes and so its data were discarded in the Figures. A similar low hydrogenating activity and also poor material balance was noted when tetrahydro derivatives of xylenes were injected on the iron catalyst layer. On the other hand, the *cis*-*trans* ratio obtained for the hydrogenation of *o*-xylene by ruthenium catalyst was too great to be shown within the scale given in Fig. 1. So its selectivity data were not shown there. It may be noted with rhodium catalyst that the selectivity data agree with those

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2) H. Yamamoto, M. O'hara, T. Kwan: This Bulletin, 12, 959 (1964).

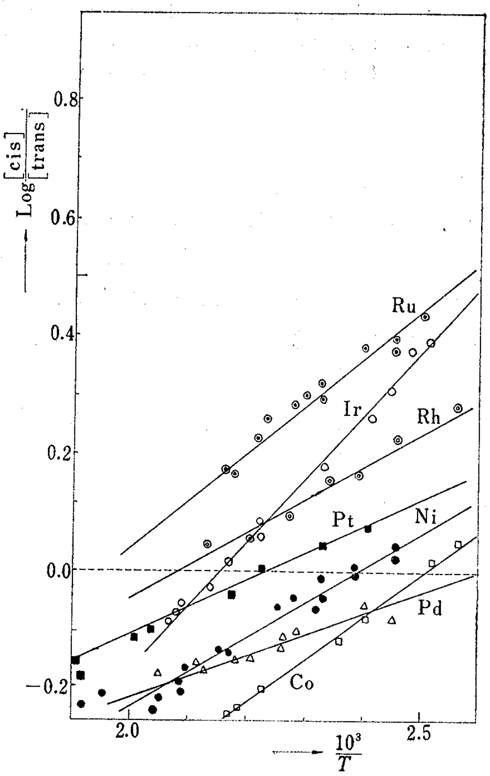

Fig. 3. The Ratio of *cis*- to *trans*-dimethylcyclohexane formed by the Hydrogenation of *p*-Xylene on Transition Metal Catalysts

obtained by Rylander[3] who studied the hydrogenation of *p*-xylene by rhodium-carbon in liquid phase.

As shown in Fig. 1 and 3, the stereoselectivity for the hydrogenation of *o*- and *p*-xylene appears to vary with the reaction temperature on each transition metal catalyst. On the other hand, as shown in Fig. 2, the *cis-trans* ratio obtained from the hydrogenation of *m*-xylene was little affected by temperature when nickel or cobalt was used as the catalyst, although the ratio was found to be dependent on temperature with the other catalysts. In spite of some difference in temperature dependencies, it is apparent that the selectivity for the formation of *trans*-dimethylcylohexane is of the following sequence:

Pd>Co>Ni>Pt>Rh>Ir>Ru for *o*-xylene
Rh>Pt~Ru>Co~Ni>Ir for *m*-xylene
Co>Pd>Ni>Pt>Rh>Ir>Ru for *p*-xylene

The selectivity appeared to be in the following order, when the hydrogenation of three xylene isomers were compared against metals.

*p*- > *o*- > *m*-xylene on Ni, Co, Pt and Pd
*p*- > *m*- > *o*-xylene on Ir, Rh and Ru

Since the *cis-trans* isomerization reaction of the product cycloalkane was found to proceed to the extent of only a few % under the same experimental condition as used for the hydrogenation of xylenes, the selectivity sequence shown above should be the result of kinetic control and inherent to the nature of the catalyst metals.

## Discussion

The mechanism of the formation of *trans* isomers from xylenes by the way of isomerization and desorption of tetrahydro derivatives has been suggested by Siegel.[4] If such steps are assumed to determine the rate of the formation of *trans* isomers, the stereoselectivity may be increased for the formation of *trans* isomers with increasing the easiness of isomerization or desorption of tetrahydro derivatives.

The following activity sequence for olefin isomerization is known with transition metal catalysts at 100°.

Fe~Ni~Rh>Pd>Ru>Pt>Ir

The chance that ethylene will undergo desorption rather than hydrogenation is known to be of the sequence :

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[3] P. N. Rylander, D. S. Steele : Engelhard Ind. Tech. Bull., **3**, 91 (1962).

[4] S. Siegel, G. V. Smith, B. Dmuchovsky, D. Dubbell, W. Halpern : J. Am. Chem. Soc., **84**, 3136 (1963).

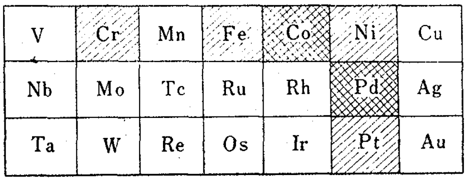
$$Ru > Rh > Ni \sim Pd > Pt > Ir$$

from the analysis of the product of the exchange reaction.[5] The selectivity for the formation of propene in the hydrogenation of propadiene to propane investigated in the temperature range 50～100° may be regarded as the another example for the easiness of olefin desorption. The sequence, according to Bond,[5] is given by

$$Pd > Ni \sim Rh > Ru > Pt > Ir$$

While the activity sequence for isomerization and desorption does not parallel with each other, it is apparent that Pt and Ir are poor catalysts for the isomerization or desorption of olefin. It is interesting to note that Ir is found to be poor for the selective formation of *trans* isomer from three xylenes.

Let us discuss the mechanism of the formation of *trans* isomers through the *trans* addition of hydrogen to π-allylic intermediate. On the basis of the available data, Bond summarized the ability of the transition metals to form π-allylic complexes.[5] The result is reproduced in Fig. 4. Fig. 4 shows that cobalt and palladium readily form π-allylic complexes while ruthenium, rhodium and iridium do not know to form such complexes.*[2] The tendency agrees well with the selectivity sequence for *o*- and *p*-xylene but not for *m*-xylene.



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|---|---|---|---|---|---|---|
| V | ▨ Cr | Mn | ▨ Fe | ▩ Co | ▨ Ni | Cu |
| Nb | Mo | Tc | Ru | Rh | ▩ Pd | Ag |
| Ta | W | Re | Os | Ir | ▨ Pt | Au |

Fig. 4. The Ability of Transition Metals to Form π-Allylic Complexes after Bond[5]

▨ Few complexes known
▩ Many complexes known

As shown in Fig. 2, the formation of *trans* isomer was considerably small when *m*-xylene was injected, on any transition metal catalyst over the entire temperature range investigated. In this connection, it may be reminded*[3] that *cis*-1,3-dimethylcyclohexane is thermodynamically more stable than the *trans* counterpart in contrast to *cis*- and *trans*-1,2- or 1,4-dimethylcyclohexane. As mentioned previously,[1] the *trans* addition of hydrogen might be restricted, in the case of *m*-xylene hydrogenation, due to the axial methyl group. Thus, the stereochemical effect would have to be taken into consideration or would be expected to play a dominant role for the stereoselective formation of one of the isomers.

Summing up the discussions, it may be said that there is a certain correlation between the ability of the transition metals to form π-allylic complexes and the degree of the selective formation of *trans* isomer from *o*- and *p*-xylene isomers by the transition metal catalysts. The correlation of this kind seems to be better than that between the observed selectivity data and such physicochemical properties as sublimation energy, % *d*-character, work function, atomic radii of transition metals. However it should be pointed out that the ability of the transition metals to form π-allylic complexes is not the only factor by which the stereoselective hydrogenation of xylenes is controlled on the transition metal catalysts of group Ⅷ.

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*[2] It is also reported[6] that nickel and iron can form many π-allylic complexes in addition to palladium and cobalt.

*[3] See Table I of ref. 1).

5) G.C. Bond, P.B. Wells : Advances in Catalysis, **15**, 205 (1964), Academic Press, Inc., New York.
6) M.L.H. Green, P.L.I. Nagy : Advances in Organo Metallic Chem., **2**, 325 (1964), Academic Press, Inc., New York.