[Chem. Pharm. Bull.
15(8)1129~1137(1967)]

UDC 542.941.7 : 547.534.2.04

141. Haruhiko Yamamoto, Hiroyuki Horiguti, Kunio Noda, and Takao Kwan: Stereoselective Hydrogenation of Xylenes and Their Tetrahydro Derivatives by a Reduced Nickel Catalyst.

(*Division of Physicochemical Technology, Faculty of Pharmaceutical Sciences, University of Tokyo*[*1])

o-, *m*-, *p*-xylene and their tetrahydro derivatives were hydrogenated by a reduced nickel catalyst over the temperature range 150~250° to investigate the mechanism of the stereoselective formation of *cis* and *trans* isomer in vapor phase. The selectivity for the formation of *trans* isomer was the greatest with *p*-xylene and the smallest with *m*-xylene. More than 50% *trans* isomer was produced with *p*- and *o*-xylene but not with *m*-xylene over the entire temperature range investigated. A similar result was obtained also for the hydrogenation of dimethylcyclohexenes.

On the basis of these findings, the Horiuti-Polanyi-Siegel mechanism, as shown schematically in Fig. 6, was discussed taking into consideration various adsorbed types for the half-hydrogenated state. It was shown that the mechanism will meet some difficulties to account for the experimental results. On the other hand, the *trans* addition of hydrogen to π-allylic adsorbed species giving rise to *trans* isomer was considered to occur in particular at higher temperatures.

(Received May 27, 1966)

When disubstituted aromatic compounds are hydrogenated on the surface of metal catalysts to yield *cis* and *trans* stereoisomers, the von Auwers-Skita rule[1,2] states that *cis* isomer is predominantly formed on a platinum in acidic media while *trans* isomer is more formed in basic media, or on a nickel catalyst in vapor phase. Linstead, *et al.*,[3] studying the hydrogenation of various aromatic compounds on platinum catalyst in acidic media, thought that an aromatic ring must be hydrogenated during a single sojourn on the catalyst from the same side of the ring to produce a *cis* isomer.

During recent years, the stereoselective hydrogenation of aromatic compounds of this kind has drawn attention of many investigators. For instance, Siegel, *et al.*[4,5] found that *trans* isomer is formed even at the initial stage of the catalytic hydrogenation of xylenes and suggested on the basis of the finding that the aromatic ring must be hydrogenated stepwise with the production of various isomeric tetrahydro derivatives according to the random distribution and that the formation of *trans* isomer is attributed to the desorption of tetrahydro derivatives followed by re-adsorption in micropore of the catalyst. Siegel's treatment may imply the absence of isomerization for tetrahdro derivatives having a certain configuration (*cis* or *trans*) of methyl group against the surface and it may also assume the desorption of tetrahydro derivatives from the surface. Especially, more than 50% *trans* isomer would never be formed according to such hydrogenation mechanism.

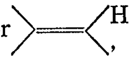
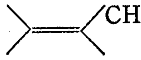
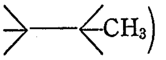
[*1] Hongo, Tokyo (山本晴彦, 堀口浩幸, 野田国男, 管 孝男).

1) A. Skita: Ann., **413**, 1 (1923).
2) K. von Auwers: *Ibid.*, **420**, 84 (1925).
3) R.L. Linstead, W.E. Doering, S.B. Davis, P. Levine, R.R. Whetstone: J. Am. Chem. Soc., **64**, 1985 (1947).
4) S. Siegel, M. Dunkel: Advances in Catalysis, **9**, 15 (1957).
5) S. Siegel, K. Ku, "Proc. 3rd Int. Congress on Catalysis," p. 1199. North-Holland Publ. Company, Amsterdam (1965).

In view of the importance of the stereoselectivity in heterogeneous catalysis, we have undertaken this problem and re-examined the stereoselective hydrogenation of *o*-, *m*- and *p*-xylenes and their tetrahydro derivatives by a reduced nickel catalyst. The hydrogenation of aromatics by metal catalysts has been investigated so far mostly in liquid phase; little is known about the stereoselectivity in vapor phase. So it would be worthy to extend this sort of study to the vapor phase.

In the previous paper,⁶⁾ the gas chromatographic pulse technique has proved to be useful and convenient for the study of hydrogenation of cyclohexadiene and cyclohexene by transition metal catalysts. The technique is also expected to provide many informations concerning the stereoselective hydrogenation of xylenes and their tetrahydro derivatives over a wide temperature range. The formation of *trans* isomer *via cis* isomer produced has often brought about some confusion in the interpretation of the selectivity data as pointed out by Burwell.⁷⁾ The detection of such reactions would most conveniently be performed again by this technique.

Experimental

Materials——*o*-, *m*-, and *p*-Xylenes were the guaranteed reagents supplied by Tokyo Kasei Co. They were at least 98% pure and used without further purification. 1,2-Dimethylcyclohexene was prepared from 2-methylcyclohexanone and purified by fractional gas chromatography. It was identified by elementary analysis (Calc.: C, 87.19; H, 12. 81, Found: C, 87.17; H, 13.09), nuclear magnetic resonance (NMR) spectra⁸⁾ (no 345 c.p.s. signal for , strong 95 c.p.s. signal for  and weak 57~50 c.p.s. signal for ) and by infrared (IR) spectra.

3,4-Dimethylcyclohexene was prepared by dehydrating 3,4-dimethylcyclohexanol and identified by elementary analysis and NMR spectra. The gas chromatographic analysis indicated that the sample contained 72% *cis* and 28% *trans*-1,2-dimethylcyclohexane when reduced on platinum carbon in ethanol at room temperature. Thus, the sample appeared to be a mixture of dimethylcyclohexene isomers containing more than 72% *cis*-3,4-(and 4,5-)dimethylcyclohexene. This will be called as "*cis*-3,4-dimethylcyclohexene" in what follows. 1,4-Dimethylcyclohexene, prepared from 2,5-dimethylcyclohexanol, was considered more than 90% pure by elementary analysis, NMR spectra and gas chromatographic analysis.

3,5-Dimethylcyclohexene, prepared in a similar way, was found to contain more than 90% *cis* isomer.

Apparatus and Procedure——The hydrogenation of xylenes and their tetrahydro derivatives were carried out by the same apparatus as reported previously.⁶⁾ Samples of nickel basic carbonate were placed in a stainless steel reaction tube (*i.d.* 3 mm.), its amount being 1.0~1.2 g. (5.0~7.0 cm. long) for the hydrogenation of xylenes and 0.3 g. (2.0~2.5 cm. long) for dimethylcyclohexenes respectively.

The basic carbonate was reduced *in situ* in a stream of hydrogen at 350° for several hours. The chromatographic column, packed with P. E. G. 6000 and Apiezone grease coated celite, was 3 m. long and kept at 90° during the experiment. The flow rate of hydrogen, used as the carrier gas, was in most cases kept constant at 80 ml./min. and the standard sample size was 2 μl.

Results

Samples of *o*-, *m*- and *p*-xylene and their tetrahydro derivatives were respectively hydrogenated on the reduced nickel catalyst. Chromatogram appeared to give usually three peaks corresponding to *trans*-, *cis*-dimethylcyclohexane and unreacted xylene when xylene was injected. Four peaks were obtained however when dimethylcyclohexene was injected. They were identified, in the order of appearance, as *trans*-, *cis*-dimethylcyclohexane, unreacted dimethylcyclohexene and xylene. In the case of *m*-xylene, the order of appearance of *cis*- and *trans*-dimethylcyclohexane was reverse. Typical chromatograms are shown in Fig. 1.

---

6) H. Yamamoto, M. O'hara, T. Kwan: This Bulletin, **12**, 959 (1964).
7) R. L. Burwell: Chem. Rev., **57**, 895 (1957).
8) O.V. Smith, P.J. Trotter: J. Org. Chem., **28**, 2450 (1963).

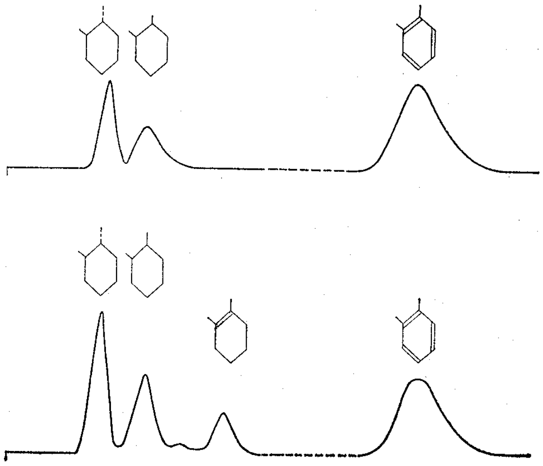
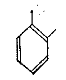
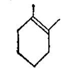


Fig. 1. Typical Reaction Chromatogram for the Hydrogenation of *o*-Xylene and 1,2-Dimethylcyclohexene on Reduced Nickel Catalyst. T=200°

Upper: Injection of 

Lower: Injection of 

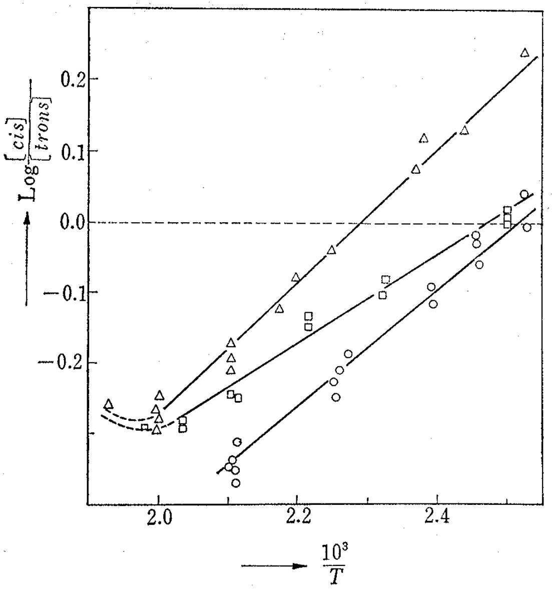
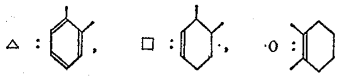


Fig. 2 Temperature Dependency of log [*cis*]/[*trans*] obtained from the Hydrogenation of *o*-Xylene and Its Tetrahydro Derivative



The stereoselectivity, as defined by the ratio of *cis*- to *trans*-dimethylcyclohexane produced was then investigated against the reaction temperature ranging from 150° to 250°. This ratio was found little dependent on the flow rate of hydrogen or on the

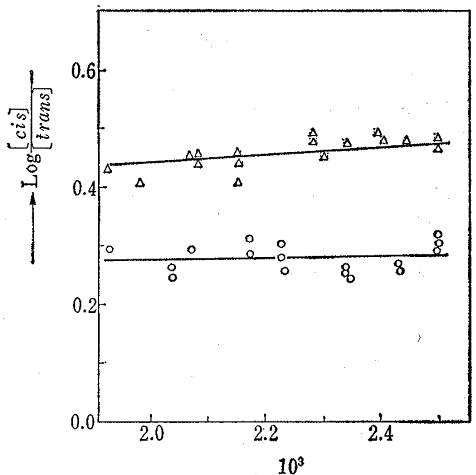
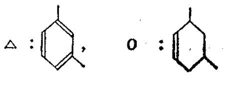


Fig. 3. Temperature Dependency of log[*cis*]/[*trans*] obtained from the Hydrogenation of *m*-Xylene and Its Tetrahydro Derivative



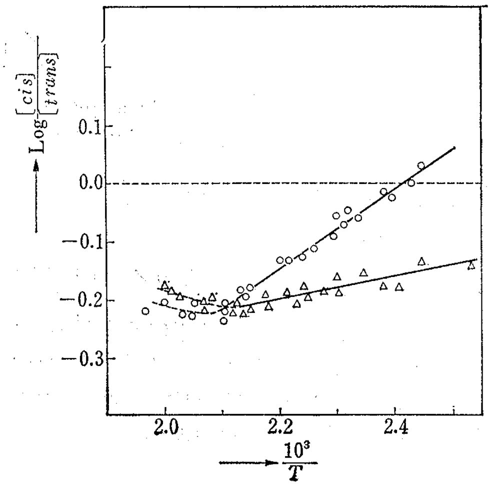
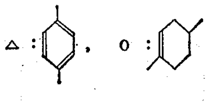


Fig. 4. Temperature Dependency of log[*cis*]/[*trans*] obtained from the Hydrogenation of *p*-Xylene and Its Tetrahydro Derivative



sample size but definitely dependent on the temperature at which the hydrogenation was taking place.[9,10] The results obtained with *o*-, *m*-, *p*-xylene and their tetrahydro derivatives are shown in Fig. 2, 3 and 4 respectively.

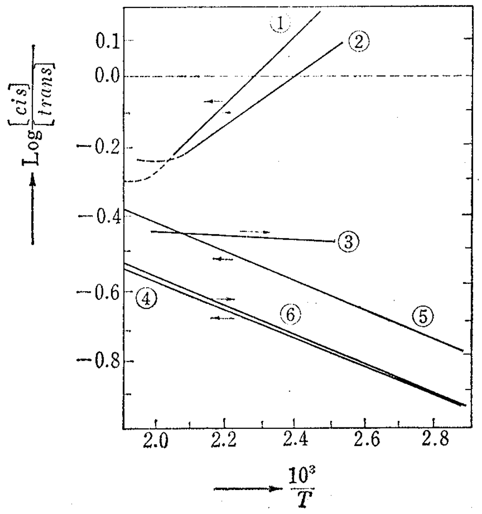


Fig. 5. Equilibrium Composition for *cis*- and *trans*-Dimethylcyclohexane (④ : 1,2-, ⑤ : 1,4-, ⑥ : 1,3-) and Observed Ratio of *cis* over *trans* (① : *o*-, ② : *p*-, ③ : *m*-)

In order to investigate if the *cis-trans* isomerization of the dimethylcyclohexane produced proceeds during the reaction, *cis*-1,2-dimethylcyclohexane was introduced on the catalyst layer at 220° under the same flow rate of hydrogen. The result indicated that only a few % *trans* isomer was formed. The injection of *cis*-1,4-dimethylcyclohexane led to a similar result, suggesting that *cis-trans* isomerization occurred to only a small extent. In Fig. 5 is shown the relative relationship between the *cis-trans* ratio observed here and the equilibrium data evaluated approximately from literatures.[11] Inspection of Fig. 5 may prove that the selectivity data in Fig. 2~4 are of kinetic nature.

It might be particularly interesting to note that *trans* isomers are formed beyond 50% at higher temperatures with *o*-, *p*-xylene and their tetrahydro derivatives while such is not the case with *m*-xylene and its tetrahydro derivative. Let us assume that the benzene ring is hydrogenated stepwise[6] and that cyclo-olefin intermediates are important precursors for the formation of *cis*- and *trans*-dimethylcyclohexane. The following reaction scheme would then be pertinent.

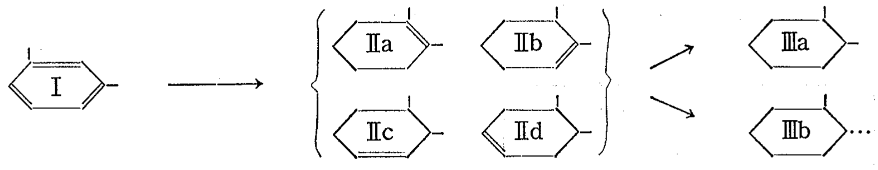


Fig. 6. Hydrogenation Scheme of *o*-Xylene to Yield *cis*- (Ⅲa) and *trans*-Dimethylcyclohexane (Ⅲb)

According to Siegel, *et al.*,[12] Ⅱa, Ⅱb, Ⅱc and Ⅱd are formed from I after the random distribution, *viz.*

Ⅱa 16.6% Ⅱb 33.3% Ⅱc 33.3% Ⅱd 16.6%

And their mechanism proposes that Ⅱc and Ⅱd give only Ⅲa and that Ⅲa and Ⅲb are produced from Ⅱa or Ⅱb through isomerization, desorption and re-adsorption. Thus, more than 50% *trans* isomer would never be formed. The experimental data obviously do not accept this mechanism at least with *o*- and *p*-xylene and their tetrahydro derivatives.

It seems very likely that tetrahydro derivatives undergo isomerization and do not maintain the concentration required by the random distribution. It may be considered[13] that Ⅱa and Ⅱb are less reactive than Ⅱd. An evidence for this was put forward using Ⅱc as an initial reactant as shown in Fig. 7. The comparison of a, b

---

[9] R.D. Schuez, L.R. Caswell: J. Org. Chem., **27**, 486 (1962).
[10] P.N. Rylander, D. Steele: Engelhard Ind. Tech. Bull., **3**, 90 (1963).
[11] A.K. Smith, B.L. Evering: J. Am. Chem. Soc., **75**, 1631 (1953).
[12] S. Siegel, G.V. Smith, B. Dmuchovsky, D. Dubbell, W. Halpern: *Ibid.*, **84**, 3136 (1962).
[13] E.W. Garbrish, S.M. Schildcrout, D.B. Patterson, C.M. Sprecher: *Ibid.*, **87**, 2932 (1965).

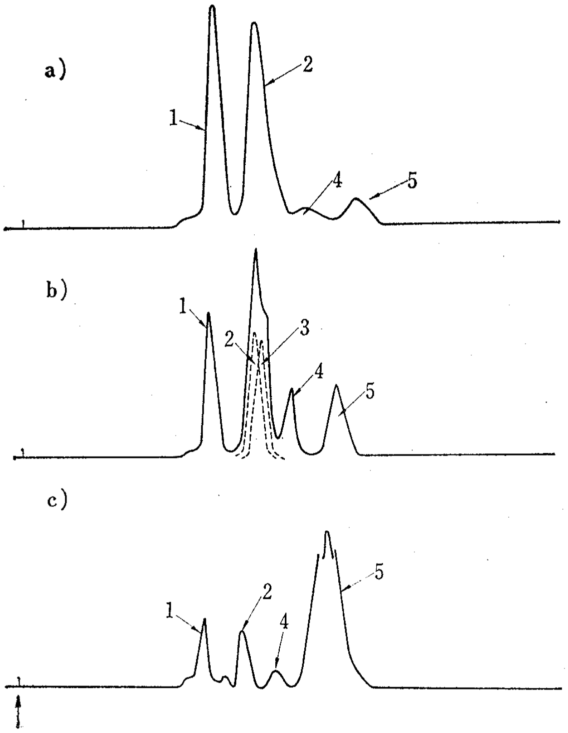


Fig. 7. Reaction Chromatogram for the Hydrogenation of Dimethylcyclohexene

a : *cis*-3,4-Dimethylcyplohexene Injected
b : *cis*-3,4-Dimethylcyclohexene Containing 10% Cyclohexylamine Injected.
c : 1,2-Dimethyl-1-cyclohexene Injected

1. *trans*-1,2-Dimethylcyclohexane
2. *cis*-1,2-Dimethylcyclohexane
3. *cis*-3,4-Dimethyl-1-cyclohexene
4. 2,3-Dimethyl-1-cyclohexene (?)
5. 1,2-Dimethyl-1-cyclohexene

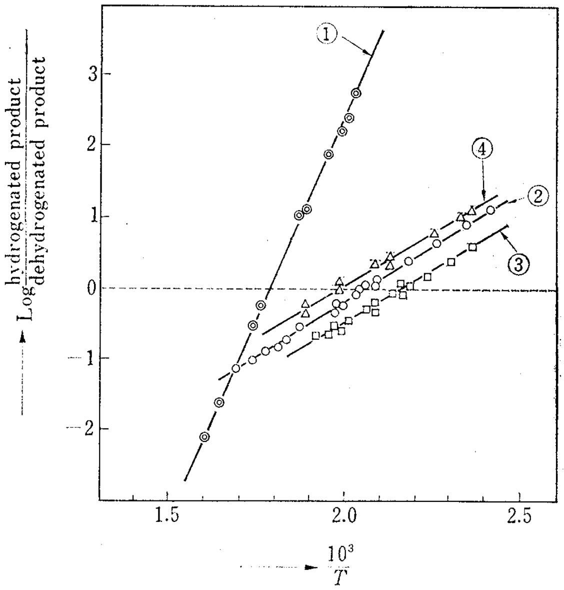


Fig. 8. Hydrogenation-Dehydrogenation Selectivity for Cycloolefins by Reduced Nickel Catalyst

1 : Benzene-Cyclohexene Equilibrium.
2 : Cyclohexene.
3 : 1,2-Dimethyl-1-cyclohexene
4 : 1,4-Dimethyl-1-cyclohexene

and c in Fig. 7 leads to the result that IIa is hydrogenated to a less extent than IIc. Moreover Fig. 7 b indicates that isomerization is taking place among tetrahydro derivatives even on a poisoned surface which possesses a low hydrogenation activity.

Table I. Heats of Formation of Some Cyclic Organic Compounds, $-\Delta H_f$ (kcal/mole)

Benzene	−19.8 a)	*o*-Xylene	−4.5 b)	*m*-Xylene	−4.1 b)	*p*-Xylene	−4.3 b)
1,3-Cyclohexadiene	−25.6 a)						
Cyclohexene	1.7 a)	1,2-Dimethyl-cyclohexene	18.3 d)	1,3-Dimethyl-cyclohexene	17.0 d)	1,4-Dimethyl-cyclohexene	17.0 d)
		2,3-Dimethyl-cyclohexene	17.0 d)				
		cis-3,4-Dimethyl-cyclohexene	(15) d)				
Cyclohexane	29.4 a)	*cis*-1,2-Dimethyl-cyclohexane	41.2 c)	*cis*-1,3-Dimethyl-cyclohexane	44.2 c)	*cis*-1,4-Dimethyl-cyclohexane	42.2 c)
		trans-1,2-Dimethyl-cyclohexane	43.0 c)	*trans*-1,3-Dimethyl-cyclohexane	42.2 c)	*trans*-1,4-Dimethyl-cyclohexane	44.1 c)

a) G.J. Janz: J. Chem. Phys., **22**, 751 (1954).
b) Lange: "Handbook of Chemistry" 10th Ed., McGraw-Hill Book Co., New York.
c) A.P.I. Table, Project 44, Carnegie Inst. Tech. Pittsburg. 1953~1961.
d) Calculated according to Allen's Bond Energy Scheme. Parameters were taken from H. Skinner: J. Chem. Soc., 4396 (1962).

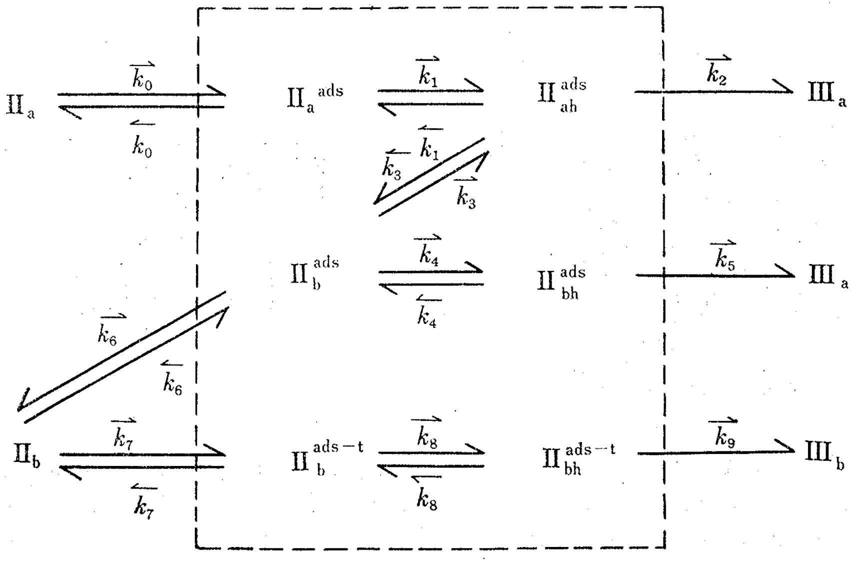
A similar isomerization reaction was found to occur under higher flow rates. Considering the electronic and steric effect of methyl groups in the substituted benzene ring, all positions on the ring do not seem equivalent. Thus the random distribution law mentioned above does not seem to be valid to account for the selective hydrogenation of xylenes at least under the present experimental conditions.

The injection of dimethylcyclohexene was found to give xylene and dimethylcyclohexane simultaneously just as in the case of cyclohexene reported in the previous paper.[6] The hydrogenation and dehydrogenation selectivity of this kind was also investigated against temperatures. The result is shown in Fig. 8.

The similarity in the hydrogenation and dehydrogenation of cyclohexene and dimethylcyclohexene may be noteworthy. For the sake of comparison the heat of formation of related cyclic organic compounds were presented in Table I.

Discussion

The formation of *trans* isomer from 1,2-dimethylcyclohexene through isomerization, desorption and re-adsorption will firstly be discussed assuming the following pseudo first order reaction scheme.



Adsorbed state

where IIa, IIb, IIIa and IIIb are already shown in Fig. 6, suffix h indicates the half-hydrogenated state and suffix t shows the adsorbed state which would ultimately form *trans* isomer.

The rates of formation of IIIa and IIIb are respectively expressed by

$$\frac{d[\mathrm{IIIa}]}{dt}=\overrightarrow{k}_2[\mathrm{II}_{ah}^{ads}]+\overrightarrow{k}_5[\mathrm{II}_{bh}^{ads}] \qquad \frac{d[\mathrm{IIIb}]}{dt}=\overrightarrow{k}_9[{}^{ads\text{-}t}_{bh}]$$

The stationary state treatment yields the following relation for the *cis-trans* ratio, S, which will be referred as "stereoselectivity."

$$\begin{aligned}S=\frac{[\mathrm{IIIa}]}{[\mathrm{IIIb}]}=\frac{\overrightarrow{k}_4}{\overrightarrow{k}_6}&\left\{\left(1+\frac{\overleftarrow{k}_6}{\overrightarrow{k}_7}+\frac{\overleftarrow{k}_6}{\overrightarrow{k}_7}\cdot\frac{\overleftarrow{k}_7}{\overrightarrow{k}_8}+\frac{\overleftarrow{k}_6}{\overrightarrow{k}_7}\cdot\frac{\overleftarrow{k}_7}{\overrightarrow{k}_8}\cdot\frac{\overleftarrow{k}_8}{\overrightarrow{k}_9}\right)\Big/\left(1+\frac{\overleftarrow{k}_4}{\overrightarrow{k}_5}\right)\right\}\\&+\frac{[\mathrm{II}_a^{ads}]}{[\mathrm{II}_b^{abs}]}\cdot\frac{\overrightarrow{k}_1}{\overrightarrow{k}_6}\left\{\left(1+\frac{\overleftarrow{k}_6}{\overrightarrow{k}_7}+\frac{\overleftarrow{k}_6}{\overrightarrow{k}_7}\cdot\frac{\overleftarrow{k}_7}{\overrightarrow{k}_8}+\frac{\overleftarrow{k}_6}{\overrightarrow{k}_7}\cdot\frac{\overleftarrow{k}_7}{\overrightarrow{k}_8}\cdot\frac{\overleftarrow{k}_8}{\overrightarrow{k}_9}\right)\Big/\right.\\&\left.\left(1+\frac{\overleftarrow{k}_1}{\overrightarrow{k}_2}\right)\right\}\end{aligned}$$

Four special cases will then be taken into consideration.

Case 1. The rate of hydrogenation of Ⅱ is greater than that of isomerization of Ⅱ, or $\vec{k}_2 \gg \overleftarrow{k}_3$. Evidently, Ⅲa is the main product, and so the case is apart from our problem.

Case 2. The rate of desorption of Ⅱ is smaller than that of the hydrogenation of Ⅱ or $\vec{k}_4 \cdot \vec{k}_5/\overleftarrow{k}_4 > \vec{k}_6$. In this case, the first term of the right hand side (r.h.s.) of the above equation for S is greater than $\vec{k}_5/\vec{k}_6 \cdot \vec{k}_4/\overleftarrow{k}_4$, and so S should be greater than unity. Thus, more than 50% formation of *trans* isomer, as actually observed, would never be expected.

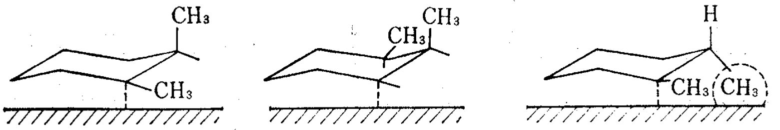
Case 3. The hydrogenation of the half-hydrogenated species is rate-controlling, or $\vec{k}_2$, $\vec{k}_5$ and $\vec{k}_9$ are very small compared with the others.

This may correspond to the Horiuti-Polanyi mechanism. Then, S may be simplified as

$$S=\frac{\vec{k}_5}{\vec{k}_9}\cdot\frac{K_4}{K_6\cdot K_7\cdot K_8}+\frac{\vec{k}_2}{\vec{k}_9}\cdot\frac{1}{K_3\cdot K_6\cdot K_7\cdot K_8}$$

where K_i represents $\vec{k}_i/\overleftarrow{k}_i$.

The half-hydrogenated state of the type Ⅱ_{bh1}^{ads}, Ⅱ_{ah1}^{ads} or $\text{Ⅱ}_{bh1}^{ads\text{-}t}$ (Fig. 9) will be investigated. Perhaps, Ⅱ_{ah1}^{ads} or Ⅱ_{bh1}^{ads} would be more stable than $\text{Ⅱ}_{bh1}^{ads\text{-}t}$ ($K_4/K_6K_7K_8$, $1/K_3K_6K_7K_8 > 1$), because the interaction between the catalyst surface and the underside methyl group, often called as "steric approach control," may be operative.

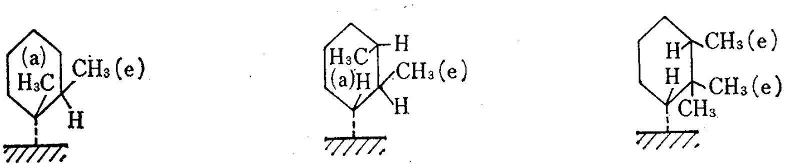


Ⅱ_{ah1}^{ads} Ⅱ_{bh1}^{ads} $\text{Ⅱ}_{bh1}^{ads\text{-}t}$

Fig. 9. Half-hydrogenated State showing "Steric Approach Control"

As the last hydrogenation steps are similar in nature, $\vec{k}_5/\vec{k}_9$ or $\vec{k}_2/\vec{k}_9$ would be nearly epual to unity. So *cis* isomer may be formed more readily than *trans* isomer.

On the other hand, the half-hydrogenated species of the type Ⅱ_{ah2}^{ads}, Ⅱ_{bh2}^{ads} or $\text{Ⅱ}_{bh2}^{ads\text{-}t}$ as shown in Fig. 10, might exist on the surface. As these adsorbed species attach to the catalyst surface at the direction of equatorial, they may have the similar stability with the free isomer produced due to the less interaction between the catalyst surface and the methyl group. The interaction of this type may correspond to so-called "product development control," and could explain the predominant formation of *trans* isomer. In this case, $K_4/K_6K_7K_8$ and $1/K_3K_6K_7K_8$ would probably have the same temperature dependency as the *cis-trans* ratio in equilibrium. The hydrogenation steps 2, 5 and 9 are similar with each other and so $\vec{k}_2/\vec{k}_9$ and $\vec{k}_5/\vec{k}_9$ may not be so sensitive to temperature. Consequently, S is expected to have the same temperature dependency in the sense of positive or negative as that of the *cis-trans* ratio in equilibrium. Since the experimental results have shown the reverse temperature dependency, the half-hydrogenated state referred in Fig. 10 does not seem to account for the observed selectivity data.



$\mathrm{II}^{ads}_{ah\,2}$ $\mathrm{II}^{ads}_{bh\,2}$ $\mathrm{II}^{ads}_{bh\,2}$

Half-hydrogenated State showing Similar Stability to Final Product

Case 4. Mention will be made to the case where desorption rate is not much different or competing with the last step of the hydrogenation.

The consideration shown above indicated that more than 50% *trans* isomer may be formed if II^{ads}_{ah2}, II^{ads}_{bh2} and $\mathrm{II}^{ads\text{-}t}_{bh2}$ are present on the surface. However, such explanation failed to account for the other experimental fact, *viz.* the temperature dependency of the formation of *cis* and *trans* isomers.

Suppose now that the rate controlling step is changing from such process as isomerization or desorption of II to the hydrogenation of half-hydrogenated species. The temperature dependency, even if in such case, is again expected to be parallel with that of the *cis–trans* ratio in equilibrium. The experimental result was not so. The first term of the r.h.s. of the selectivity expression may be expressed approximately as

$$\frac{\vec{k}_5}{\vec{k}_6}\cdot \mathrm{K}_4 + \frac{\vec{k}_5}{\vec{k}_7}\cdot\frac{\mathrm{K}_4}{\mathrm{K}_6} + \frac{\vec{k}_5}{\vec{k}_8}\cdot\frac{\mathrm{K}_4}{\mathrm{K}_6\cdot\mathrm{K}_7} + \frac{\vec{k}_5}{\vec{k}_9}\cdot\frac{\mathrm{K}_4}{\mathrm{K}_6\cdot\mathrm{K}_7\cdot\mathrm{K}_8}$$

If it is assumed that $\vec{k}_5/\vec{k}_9$ is equal to unity and that $\mathrm{K}_4/\mathrm{K}_6\mathrm{K}_7\mathrm{K}_8$ is equal to the value of the *cis–trans* ratio in equilibrium, $\vec{k}_5/\vec{k}_9\cdot\mathrm{K}_4/\mathrm{K}_6\mathrm{K}_7\mathrm{K}_8$ should then be equal to the value of the *cis–trans* ratio in equilibrium. Therefore, $\vec{k}_5/\vec{k}_9\cdot\mathrm{K}_4/\mathrm{K}_6\mathrm{K}_7\mathrm{K}_8$ is calculated to be 0.32 at 180° (Fig. 2). On the other hand, as the observed S is 0.56 at the same temperature, the sum of all terms of S except $\vec{k}_5/\vec{k}_9\cdot\mathrm{K}_4/\mathrm{K}_6\mathrm{K}_7\mathrm{K}_8$ should be 0.24. Provided that the largest term among all is $\vec{k}_5/\vec{k}_6\cdot\mathrm{K}_4$, the term is expected to be less than 0.2, that is, the desorption rate may be five times greater than the hydrogenation rate. As such situation is close to pre-equilibrium state, $\vec{k}_5/\vec{k}_9\cdot\mathrm{K}_4/\mathrm{K}_6\mathrm{K}_7\mathrm{K}_8$ will determine the value of S. The observed temperature dependency is thus unable to be explained.

Let us discuss other possible mechanisms for the formation of *cis* and *trans* isomer in which the addition of hydrogen from both sides of the ring plane is involved. There seems to be two possible intermediates on the surface. One is dissociatively adsorbed species as proposed by Burwell.[14] The other is π-allylic adsorbed species as maintained by Rooney.[15]

As has been already shown in Fig. 8, the injection of dimethylcyclohexene gave both hydrogenated and dehydrogenated products. Therefore, it would be natural to assume that a kind of dehydrogenated species, which would ultimately be converted to aromatics, will be formed on the surface with increasing temperature. It seems unlikely that the dissociatively adsorved species, reserving olefinic bond, is stable and

---

[14] R.L. Burwell, Jr., B.K.S. Smith, H.C. Rowlinson: J. Am. Chem. Soc., **79**, 5142 (1957).
[15] J.J. Rooney, G. Webb: J. of Catalysis, **3**, 488 (1964).

abundant on the surface as compared with π or π-allylic complex,[*2] and that the addition of hydrogen occurs to the position which does not interact with the surface of catalyst.

The experimental result that *cis* isomer is rich in the case of *m*-xylene as compared with *o*- or *p*-xylene might be explainable in such a way that *trans* addition is somewhat restricted due to the axial methyl group.

The formation of large amounts of *trans* isomer by the reduced nickel catalyst at higher temperature (150~250°) could be explained if π-allylic adsorbed species is allowed to be the main reaction intermadiate. But there is no direct proof that such an intermediate is present in the hydrogenation of xylene and that the formation of small amounts of *trans* isomer at lower temperatures or in liquid phase does not obey the mechanism advocated by Siegel which involves isomerization and desorption of tetrahydro derivatives.

It is the opinion of the authors that the half-hydrogenated state hypothesis to interpret the stereoselectivity in interest meets some difficulties to account for the experimental results and that the pathway to *cis* and *trans* isomers would probably not remain constant over the wide temperature range.

The authors wish to thank Dr. S. Nishimura for his valuable discussions. The research was supported in part by a grant from the Ministry of Education to which the authors' grateful acknowledgments are made.

[*2] The presence of π-allylic intermediate was shown kinetically by Sachtler, *et al.* with propylene adsorbed on an oxide catalyst (See Ref. 5) p. 252).