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135. Haruhiko Yamamoto, Makoto O'hara, and Takao Kwan: On the Hydrogenation and Dehydrogenation of Cyclohexene and 1,3-Cyclohexadiene on Transition Metals by Gas Chromatographic Pulse Technique.

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The gas chromatographic pulse technique, when applied to the study of heterogeneous catalysis,[1] is often characterized by a certain restriction for the detailed kinetic analysis due to the ill-defined reaction circumstance. Nevertheless, the technique may bring forth a prompt and useful information concerning the selectivity of a catalyst and particularly has a merit of enabling us to follow a rapid reaction rate which is extremely difficult to follow by a static method. It is the purpose of the present paper to investigate first the equilibrium reaction of the hydrogenation of benzene to give cyclohexane on a highly active catalyst and second to obtain kinetic data about the reactions of cyclohexene and of 1,3-cyclohexadiene as well on reduced transition metals by taking advantage of this technique.

The reactions were chosen partly because of the well established knowledge on equilibrium data. Main interest was placed however on the selectivity of the catalysts for the two reactions: hydrogenation and dehydrogenation, when cyclohexene or 1,3-cyclohexadiene was injected into the reactor. The investigations conducted along this line proved that the technique provides as expectedly a valuable information about the catalyst selectivity. The interpretation of the result was carried out with main emphasis on the temperature dependence of the selectivity.

Experimental

Shimadzu gas chromatograph of the type GC-IB was used for the purpose. A portion of the chromatographic column of stainless steel tubing was employed as the reactor. It was connected to the chromatographic column consisted of 3 meter lengths packed with PEG 6000 (polyethylene glycol) and high vacuum grease coated celite. Ni, Co and Fe in the form of basic carbonate were respectively filled in the reactor tube (about 3 cm. long with sectional area 0.25 cm^2), inserted in an electrically heated jacket and then reduced *in situ* in a stream of hydrogen. The reduction was carried out at 400° for 7 hr. for Ni and Co and at 450° for about 60 hr. for Fe. Pt-alumina catalyst used for petroleum reforming was also investigated; it was pretreated at 400° for 5 hr. similarly as above.

Benzene, 1,3-cyclohexadiene, cyclohexene and cyclohexane supplied by Tokyo Kasei Co. were used. The gas chromatographic analysis indicated that cyclohexene was 99% pure while 1,3-cyclohexadiene contained benzene and cyclohexene amounting respectively 6%. These samples were used without further purification.

A sample of hydrocarbon ranging from 1 to 5 μl. was injected in a stream of H_2 carrier to pass through the reactor containing a given catalyst kept at a desired temperature. The flow rate of H_2 could be varied from 20 to 200 ml./min. In most experiments the flow rate was 100 ml./min. with inlet H_2 pressure of 1.5 atm. which corresponded to a contact time of about 0.3 sec. A typical chromatogram of the hydrogenation and dehydrogenation products for 1,3-cyclohexadiene observed on reduced Fe is shown in Fig. 1.

The temperature of the reaction here was successively raised from left to right and it can be seen that the peak of benzene grows while that of cyclohexene decays with increasing temperature. The detection of the resultant was carried out by the thermal conductivity gauge. The area under a peak was taken as the amount of a respective component present.

[*1] Hongo, Tokyo (山本晴彦, 小原 誠, 管 孝男).

[1] Microcatalytic-chromatographic technique as investigated first by R. J. Kokes, H. Tobins Jr., P. H. Emmett: J. Am. Chem. Soc., 77, 5860 (1956).

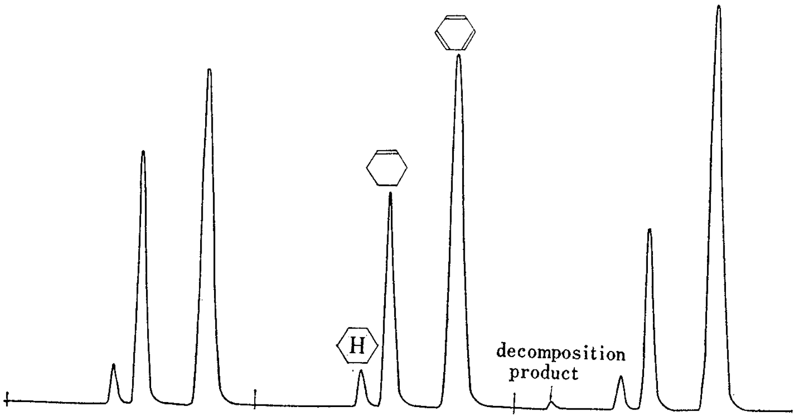

Fig. 1. Typical Chromatogram for the Reactions of 1,3-Cyclohexadiene on Reduced Iron kept in a Stream of Hydrogen

Flow rate of hydrogen: 69 ml./min.
Column packing: Polyethylene glycol 1.5 m. +Apiezon grease 1.5 m.
Column temp.: 84° Sample size: 1 μl.
Reaction temp.: from left to right 304, 312, 324°.

Results

Equilibration of Benzene-Cyclohexane Reaction

The gas chromatographic pulse technique, when applied to heterogeneous reaction, may determine in principle the equilibrium position of a reaction provided that the reaction is reversible and proceeds rapid enough compared with the movement of the reacting zone. Thus, the *para-ortho* hydrogen conversion was able to lead to an equilibrium in this laboratory on manganous chloride-coated alumina column.[2] The situation of this sort would probably be reached with difficulty in the case of the catalytic hydrogenation-dehydrogenation reaction. An attempt was made therefore, by using a highly active hydrogenation catalyst, to investigate the benzene-cyclohexane equilibrium in the light of the thermodynamical data available in the literature.[3]

Platinum-alumina catalyst supplied by Esso was employed for this purpose. A sample of cyclohexane, cyclohexene, 1,3-cyclohexadiene or benzene was injected in a stream of hydrogen to pass through the reactor tube containing platinum-alumina at the temperature range 150~300°. In any case the reaction products were consisted exclusively of cyclohexane and benzene while the variables such as the flow rate, sample size, reaction temperature and so on were widely varied. The ratio of cyclohexane to benzene was found to depend largely upon the reaction temperature only.

On the other hand, it is necessary to know the partial pressure of hydrogen in the reactor to evaluate the equilibrium constant of the reaction, $C_6H_6+3H_2 \rightleftharpoons C_6H_{12}$, from the observed ratio of cyclohexane to benzene. It seems very probable however in the present technique that the partial pressure of hydrogen in the reactor varies from place to place and is never constant. Thus, the value of hydrogen pressure was accepted conventionally as the equilibrium one when it yielded the equilibrium constant consistent with the value calculated from the thermodynamical data. It was found in this way that 0.52 atm. hydrogen was the average equilibrium pressure. Since the inlet pressure of hydrogen was 1.5 atm., the partial pressure of hydrocarbons was expected to be about 1 atm. during the reaction.

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2) K. Fujita, T. Kwan: Japan Analyst, 12, 15 (1963); S. Furuyama, T. Kwan: J. Phys. Chem., 65, 190 (1961).

3) G. I. Janz: J. Chem. Phys., 22, 751 (1954).

In Fig. 2 the logarithm of the ratio of cyclohexane to benzene produced (denoted by log A/B) is plotted against $1/T$. As indicated by the double circles, the plots were linear and its slope was found to be 51 kcal./mole in agreement with the heat of hydrogenation of benzene to give cyclohexane.

A straight line was drawn, on the other hand, for log A/B *vs.* $1/T$ so as to fit in the equilibrium data of the literature³⁾ by assuming the equilibrium pressure to be 0.52 atm. for hydrogen. The agreement of the observed values with the calculated one was satisfactory over a wide range of temperature. Quite apart from the numerical values, it seems very likely that the equilibration of benzene–cyclohexane reaction is effectively attained by the pulse technique.

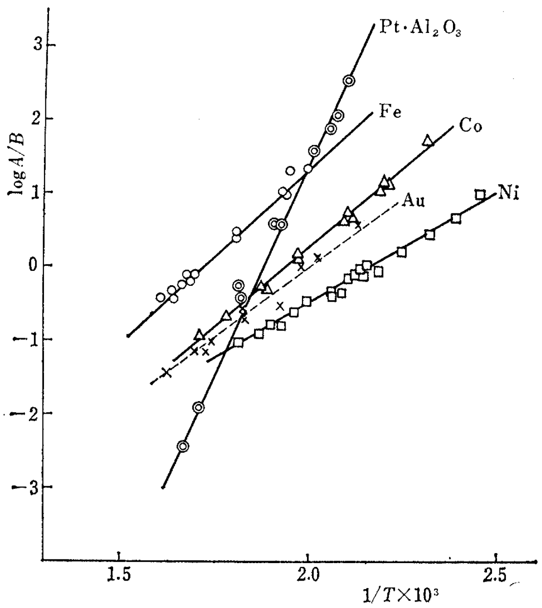

Fig. 2. The Plot of log V_A/V_B *vs.* $1/T$ for the Hydrogenation–Dehydrogenation of Cyclohexene on Reduced Metals

Hydrogenation-Dehydrogenation of Cyclohexene on Reduced Nickel, Cobalt, and Iron

In contrast with the case of platinum–alumina, neither benzene nor cyclohexane was found to react appreciably on reduced nickel, cobalt and iron under the same experimental condition. The hydrogenation and dehydrogenation of cyclohexene however readily took place on these metals. The degree of conversion of cyclohexene to cyclohexane and benzene were dependent upon the reaction temperature and appeared rather insensitive to the flow rate of hydrogen. At 200° the degree of conversion was 80% on nickel, 40% on cobalt and about 7% on iron. The sequence of the catalyst activity was hence Ni>Co>Fe.

The plot of log A/B *vs.* $1/T$ is shown in Fig. 2 for the three metals. As shown in Fig. 2, the plot gave a straight line on any metal but with different slopes. The slope was estimated to be 13.6, 19.5, and 22.4 kcal./mole respectively for nickel, cobalt and iron. It was noted that the relative selectivity of the three metals for the dehydrogenation of cyclohexene is in parallel with the sequence of the activity. The reversal relation will of course be found if the relative selectivity for the hydrogenation is compared with the conversion activity.

It is surprising to see that the initial hydrogenation and dehydrogenation rates of cyclohexene to give cyclohexane and benzene obtained by Kemball, *et al.*⁴⁾ on evaporated gold films by a static method, when plotted in the present manner, give rise to a similar straight line. Gold is known to be a very poor hydrogenating catalyst.⁵⁾ Nevertheless, the ratio of the hydrogenating selectivity to the dehydrogenating one appeared to fall in among the three transition metals.

Hydrogenation-Dehydrogenation of 1,3-Cyclohexadiene on Reduced Nickel, Cobalt, and Iron

The chromatogram yielded three or four peaks depending upon the reaction temperature when 1,3-cyclohexadiene was injected onto these metal catalysts. The appearance of the peak also depended upon the kind of the catalyst; unreacted 1,3-cyclohexadiene

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4) J. Erkelens, C. Kemball, A. K. Galway : Trans. Faraday Soc., **59**, 1181 (1963).

5) R. J. Mikovsky, M. Boudart, H. S. Taylor : J. Am. Chem. Soc., **76**, 3814 (1954); W. M. H. Sachtler, N. H. de Boer : J. Phys. Chem., **64**, 1579 (1960).

appeared only slightly on nickel whereas four peaks corresponding cyclohexane, cyclohexene, 1,3-cyclohexadiene and benzene were found on cobalt and iron respectively. The degree of conversion of 1,3-cyclohexadiene to cyclohexane, cyclohexene and benzene was found to be the sequence, Ni>Co>Fe similarly as the case of cyclohexene injection.

The plot of log A/B against $1/T$ in the case of nickel is shown in Fig. 3. As can be seen from Fig. 3, the plot gave a break near 160°, being consisted of two linear portions. Below 160° the slope, *i.e.* the temperature coefficient was very small while above 160° it exceeded a few over 10 kcal./mole, being hence nearly coincident with that of cyclohexene injection. The dotted line of Fig. 3 indicates those plots when cyclohexene was injected instead of 1,3-cyclohexadiene. It may be considered from the kinetic viewpoint that at higher temperatures the hydrogenation-dehydrogenation of 1,3-cyclohexadiene takes place similar to cyclohexene.

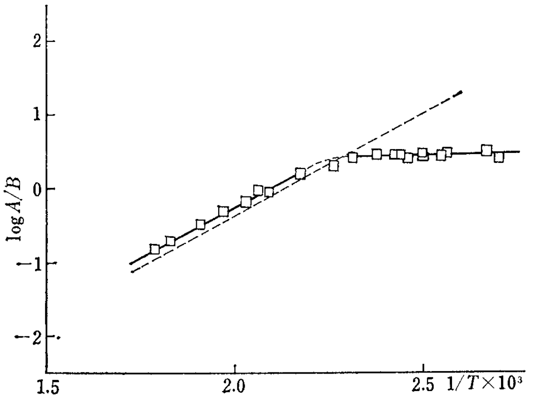


Fig. 3. The Hydrogenation-Dehydrogenation of 1,3-Cyclohexadiene on Reduced Nickel. Dotted Line indicates the Same Plot for Cyclohexene Injection

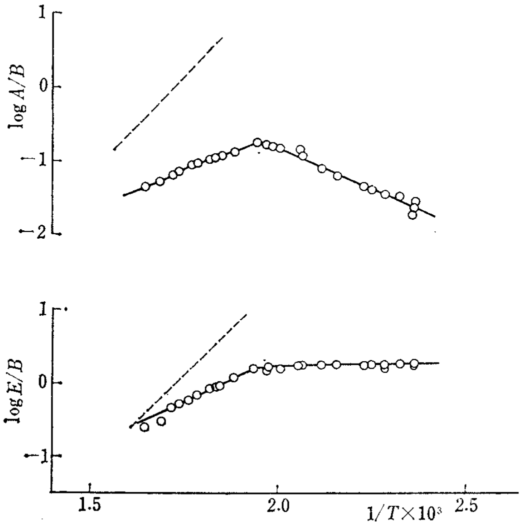
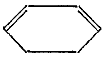
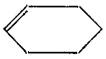
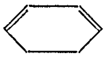
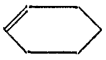


Fig. 4. The Hydrogenation-Dehydrogenation of 1,3-Cyclohexadiene on Reduced Iron. Dotted Lines indicate log V_A/V_B *vs.* $1/T$ Relation for Cyclohexene Injection

Fig. 4 indicates the reaction of 1,3-cyclohexadiene obtained on reduced iron. The dotted line indicates again the plot of log A/B *vs.* $1/T$ for cyclohexene injection. The catalyst activity of iron to give cyclohexane was found to be considerably low compared with that on nickel; the main hydrogenated product was cyclohexene. Therefore, in Fig. 4 various ratios of the products were also plotted against $1/T$.

Table I. The Comparison of the Composition of Products for the Reaction of 1,3-Cyclohexadiene and Cyclohexene on Reduced Iron

Reaction temp. (°C)	Reactant	Composition of resultant[a] (%)			
					
200		4.5	61.4	0	34.1
		7.0	93.0	0	0
300		3.2	32.6	0	64.2
		9.0	84.0	0	7.0

a) Corrected for the initial composition.

Two features may be inferred from Fig. 4. First, there existed again a break in the plot of log A/B *vs.* $1/T$ although it was found at a much higher temperature (240°) compared with that on nickel. Second, the reaction of 1,3-cyclohexadiene appeared to be rather dissimilar with that of cyclohexene at least under the temperature range investigated; this was born out from the disagreement of the plot between 1,3-cyclohexadiene and cyclohexene at all the temperatures. In Table I, the composition of the products was compared with regard to the reaction of 1,3-cyclohexadiene and cyclohexene.

Reactions of Cyclohexene on Nickel in the Absence of Hydrogen

The gas chromatographic pulse technique readily enables us to follow catalysed reactions occurring in different carrier gases. It was shown in Fig. 5 that cyclohexene reacts so poorly on reduced nickel kept in a stream of helium; the hydrogenation of cyclohexene decreased rapidly by switching the carrier from hydrogen to helium. Since the amounts of presorbed hydrogen can be estimated to be much smaller than those of cyclohexene injected and furthermore the amounts of hydrogen transferred to cyclohexane exceed those expected from the intermolecular transfer of cyclohexene, it would be quite natural to presume that the hydrogenation occurs *via* gaseous hydrogen. The disproportionation of cyclohexene molecules to produce cyclohexane and benzene seems to be untenable or less important. A similar point of view has been put forward by Gryaznov and Yagodovskii⁶⁾ on the basis of the kinetic arguments.

As shown also in Fig. 5, the conversion activity of cyclohexene to give cyclohexane and benzene appeared to decrease down to nearly zero in the absence of hydrogen. It is of interest to note that the catalyst selectivity for the formation of cyclohexane increases, after a certain period, in contrast with the decrease in the conversion activity.

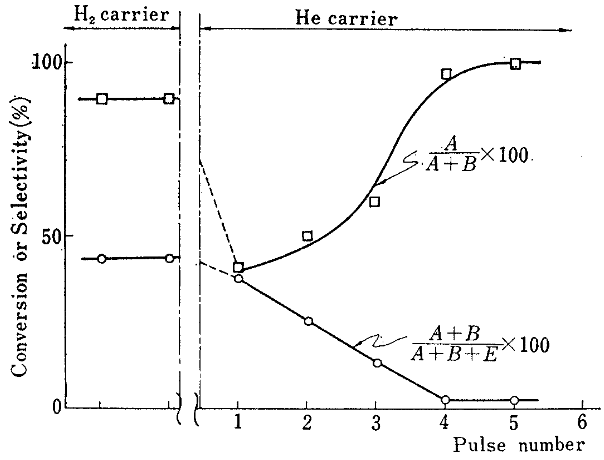


Fig. 5. The Time Dependence of the Reactions of Cyclohexene in a Stream of Helium on Reduced Nickel

Reaction temp.: 150° Sample size: 5 μl.
Flow rate of helium: 83 ml./min.

It is expected that the surface of nickel is progressively covered by C_6H_X formed by the reaction

$$C_6H_{10} \longrightarrow C_6H_X(a)+(10-x)H(a)$$

leaving a small fraction of the surface available for the chemisorption of cyclohexene. Under such condition the dehydrogenation of cyclohexene would probably be suppressed, leading apparently to the preferential formation of cyclohexane.

Discussion

The hydrogenation-dehydrogenation reaction under investigations would probably be represented by a sequence of the consecutive addition or substraction of hydrogen as below where B, D, E and A denote respectively benzene, 1,3-cyclohexadiene, cyclohexene and cyclohexane and V_{Bd}, V_{Ba}, V_{1h}, V_{2d}, etc. are the rates of the respective stage. Let us

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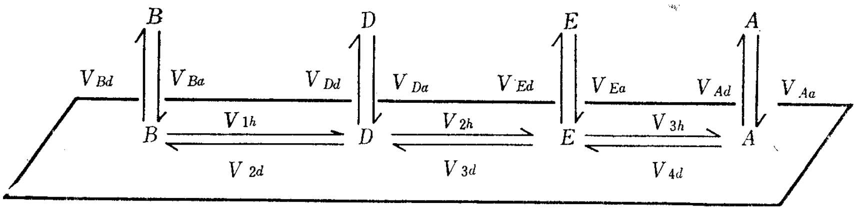
6) V.M. Gryaznov, V.D. Yagodovskii: Kin. Kata., 3, 404 (1963).



discuss first the reaction of cyclohexene on metals to get an idea about the relationship between log A/B and $1/T$. It is assumed for simplicity sake that A/B is proportional to V_A/V_B and the surface reaction is rate-determining. The reaction is also assumed to be represented by a rate proportional to the hydrogen pressure and independent of the cyclohexene.[*2]

The rate of formation of cyclohexane V_A and the rate of formation of benzene V_B are expressed, by admitting the steady state approximation, respectively as

$$V_A = V_{3h} - V_{4d} = V_{Ad} - V_{Aa}$$

$$V_B = V_{3d} - V_{2h} - (V_{Dd} - V_{Da}) = V_{2d} - V_{1h} = V_{Bd} - V_{Ba}$$

The experiment showed that neither benzene nor cyclohexane reacts appreciably on nickel, cobalt, and iron whereas 1,3-cyclohexadiene or cyclohexene does on these catalysts. The fact would mean $V_{1h}=0$ and $V_{4d}=0$. Thus,

$$V_A = V_{3h} \qquad (1)$$

On the other hand, no 1,3-cyclohexadiene was formed during the reaction of cyclohexene on metals (see Table 1). V_B may hence be given by

$$V_B = V_{3d} - V_{2h} = V_{2d} \qquad (2)$$

or by

$$V_B = V_{3d} \frac{1}{1+\frac{V_{2h}}{V_{2d}}} \qquad (3)$$

The ratio of V_A to V_B is now expressed by

$$\frac{V_A}{V_B} = \frac{V_{3h}}{V_{3d}} \left(1 + \frac{V_{2h}}{V_{2d}}\right) \qquad (4)$$

The temperature coefficient of log V_A/V_B arises from two terms : $\frac{V_{3h}}{V_{3d}}$ and $1+\frac{V_{2h}}{V_{2d}}$. In view of thermodynamical instability of 1,3-cyclohexadiene compared with any of cyclohexene and benzene, it would be expected that the temperature coefficient of the latter is much less than that of the former. Then, we have

$$RT^2 \log \frac{V_A}{V_B} = E_{3h} - E_{3d} - q \qquad (5)$$

where E_{3h} and E_{3d} are the activation energy of the stage $3h$ and $3d$ and q is the heat of chemisorption of hydrogen.

As shown in Fig. 2, the log A/B decreases with increasing temperature. $E_{3h} - E_{3d} - q$ is hence negative or E_{3h} is smaller than $E_{3d}+q$. Since the hydrogenation is exothermic and the dehydrogenation endothermic, the situation revealed in the temperature coefficient of the selectivity should be quite natural.

[*2] The rate law was assumed purely for convenience; the assumption is not necessarily required.

It is shown also in Fig. 2 that $E_{3h}-E_{3d}-q$ value differs among three metals. It may be said that the hydrogenating selectivity is the greatest on iron whereas the dehydrogenating one is so on nickel. The interpretation of such selectivity would require further postulates about the substrate-surface interaction. It might be mentioned however that the heat of chemisorption of hydrogen is of the order Ni>Co>Fe[7] in harmony with the order of the temperature coefficient under discussion.

The reaction of 1,3-cyclohexadiene will be considered next. The rate of formation of cyclohexane is

$$V_A=V_{2h}-V_{3d}-(V_{Ed}-V_{Ea})=V_{3h}-V_{4d}=V_{Ad}-V_{Aa}$$

and the rate of formation of benzene

$$V_B=V_{2d}-V_{1h}=V_{Bd}-V_{Ba}$$

No appreciable reaction of either benzene or cyclohexane may lead to the relations: $V_{1h}=0$ and $V_{4d}=0$. Hence we have

$$V_A=V_{2h}\frac{1}{1+\frac{V_{3d}}{V_{3h}}+\frac{V_{Ed}}{V_{3h}}-\frac{V_{Ea}}{V_{3h}}} \tag{6}$$

$$V_B=V_{2d} \tag{7}$$

Consequently, the ratio V_A/V_B is given by

$$\frac{V_A}{V_B}=\frac{V_{2h}}{V_{2d}}\left(\frac{1}{1+\frac{V_{3d}}{V_{3h}}+\frac{V_{Ed}}{V_{3h}}-\frac{V_{Ea}}{V_{3h}}}\right) \tag{8}$$

On the other hand, experiments have shown that no cyclohexene is formed on nickel. So $V_{Ed}=V_{Ea}=0$. V_A can then be given by

$$V_A=V_{2h}\frac{1}{1+\frac{V_{3d}}{V_{3h}}} \tag{9}$$

so that the ratio is expressed by

$$\frac{V_A}{V_B}=\frac{V_{2h}}{V_{2d}}\cdot\frac{1}{1+\frac{V_{3d}}{V_{3h}}} \tag{10}$$

Let us discuss the temperature dependency of equation (10), confining ourselves to two limiting cases.

Case 1. $1\gg V_{3d}/V_{3h}$. We have then

$$\frac{V_A}{V_B}=\frac{V_{2h}}{V_{2d}} \tag{11}$$

Case 2. $1\ll V_{3d}/V_{3h}$. Equation (10) is now approximated by

$$\frac{V_A}{V_B}=\frac{V_{2h}}{V_{2d}}\cdot\frac{V_{3h}}{V_{3d}} \tag{12}$$

The temperature dependency of equation (11) or equation (12) is now ready for formulations. As already mentioned, the temperature dependency of V_{2h}/V_{2d} has been supposed

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[7] T. Kwan: Advances in Catalysis, **6**, 67 (1954).

to be smaller than that of V_{3h}/V_{3d}. Thus, the temperature dependency of Case 2 should be greater than that of Case 1 in respect to the absolute value.

Fig. 3 has shown that the temperature coefficient of log A/B is greater at higher temperatures than that at lower temperatures in its absolute value. Thus, equations (11) and (12) seem likely to correspond to the ratio at lower and higher temperatures respectively. Since A/B or the left of equations (11) and (12) is far greater than unity at lower temperatures and less than unity at higher temperatures, the correspondence may be sound enough.

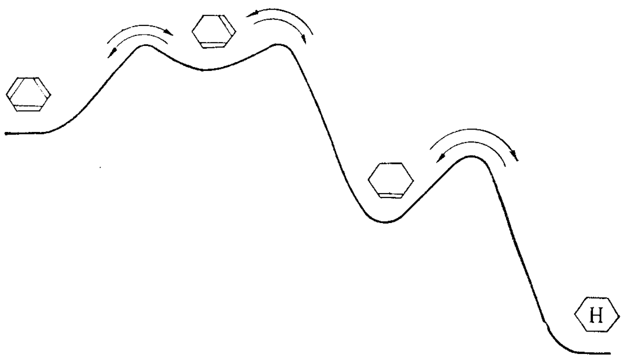

Fig. 6. Schematic Representation of the Potential Energy Level Diagram for the Reaction of Benzene, 1,3-Cyclohexadiene, Cyclohexene and Cyclohexane on Reduced Metals

The temperature dependency of the rate of hydrogention-dehydrogenation reaction of 1,3-cyclohexadiene could be guessed more conveniently by a schematic potential energy diagram. The diagram is shown in Fig. 6 in which the potential energy of benzene, 1,3-cyclohexadiene, cyclohexene and cyclohexane at the chemisorbed layer was drawn against the reaction coordinate.

1,3-Cyclohexadiene is thermodynamically unstable compared with either benzene or cyclohexene. A similar situation was assumed to hold also at the chemisorbed layer. So it may be converted to benzene and cyclohexene with little difference in the activation energy. At lower temperatures what is actually observed is the hydrogenation of 1,3-cyclohexadiene to cyclohexene and the dehydrogenation of 1,3-cyclohexadiene to benzene. The small temperature coefficient observed at lower temperatures in Fig. 3 may probably be ascribed to such a situation.

The argument is confirmed in the plot of log E/B *vs.* $1/T$ obtained on reduced iron where the catalyst activity is so low that the main hydrogenated product is cyclohexene (Fig. 4).

On the other hand, the approximate agreement of the relative selectivity as well as of the temperature coefficient of the reactions of 1,3-cyclohexadiene with those of cyclohexene at higher temperatures, as shown also in Fig. 3, may suggest that the hydrogenation of 1,3-cyclohexadiene is quick enough so that cyclohexane and benzene are formed as if originated from cyclohexene. Thus, kinetic behavior of the hydrogenation-dehydrogenation of cyclohexene and 1,3-cyclohexadiene can be explained in accordance with their thermodynamical potentials at least in a qualitative way.

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Summary

Reactions of benzene, 1,3-cyclohexadiene, cyclohexene and cyclohexane have been investigated on reduced transition metals by using a gas chromatographic pulse technique. Main interest was placed on the applicability of this technique to a prompt evaluation of the selectivity; the destination of the intermediates in benzene-cyclohexane reaction, when injected in a stream of hydrogen, has been determined by taking advantage of the technique.

The hydrogenation selectivity was found to be of the sequence Ni<Co<Fe, being reversed with the conversion activity of 1,3-cyclohexadiene or of cyclohexene to give cyclohexane and benzene. Quite synonymously the dehydrogenation selectivity was in parallel with the conversion activity. The temperature dependency of the relative selectivity was analyzed on the basis of the steady state approximation of the hydrogenation-dehydrogenation reaction. The general trend of the hydrogenation-dehydrogenation reaction of 1,3-cyclohexadiene and of cyclohexene has been successfully explained with the potential energy level diagram of the reaction.

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