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Studies Concerning the Factors Affecting the Formation of Cyclohexanone Intermediates in the Catalytic Hydrogenation of Phenols. I. Hydrogenation of *p*-Cresol over Various Pd-C Catalysts

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The catalytic hydrogenation of *p*-cresol with commercial Pd on active carbon (Pd–C), water-washed Pd-C (Pd-C–N), acid-treated Pd-C (Pd–C–A), and base-treated Pd-C (Pd–C–B) has been kinetically studied in cyclohexane as a solvent under 0.15—8.0 MPa hydrogen pressure at 80 °C. Under each reaction condition, the hydrogenation rate constants for the cresol and the ketone intermediate, k_1+k_3 and k_2, respectively, the relative reactivity of the ketone to the cresol (K) and the ratio of the adsorption coefficient of the ketone to that of the cresol (b_2/b_1) were determined on the basis of a Langmuir-Hinshelwood model. Regardless of the difference in the nature of the catalysts, hydrogenations with these catalysts always gave high selectivities of 0.85—1.0 for the formation of the ketone intermediate, and small values of 0.014—0.62 for the relative reactivity (K). The small values of K over Pd–C and Pd–C–B were shown to be mostly due to the small values of $k_2/(k_1+k_3)$. In contrast, even smaller values of K over Pd–C–N and Pd–C–A were found due to a great difference in the strength of adsorption between the cresol and the ketone intermediate. In general, both the values of K and $k_2/(k_1+k_3)$ increase with increasing hydrogen pressure. All of the experimental results show that both the alkaline impurities associated with catalyst preparation and the hydrogen pressure are the most important factors affecting the formation of the ketone intermediate.

The selectivity of metals in the catalytic hydrogenation of aromatic compounds is closely related to the selectivity for the formation of the corresponding intermediates.[1] In most cases, the amount of intermediates detectable during the course of hydrogenation is rather small, which makes it difficult to estimate the real yields of the intermediates formed on the catalyst surface and to interpret the course of the hydrogenation quantitatively.[2,3] However, in the hydrogenation of phenols the major intermediates are relatively unreactive cyclohexanones and they may accumulate in considerable amounts during the hydrogenation.[4] For this reason the hydrogenation of phenols is an excellent example for a study of the selectivity of metals for forming of the intermediate quantitatively. The selectivity for cyclohexanones in the hydrogenation of phenols is known to be greatly influenced not only by the catalyst metals employed, but also by the reaction conditions and additives.[5] Palladium catalysts have been known to be the most selective among the platinum metals for the hydrogenation of phenols to the corresponding cyclohexanones.[6] However, no detailed or quantitative studies have been carried out with respect to the factors which may affect the relative reactivity of the phenols to the intermediate ketones, such as the reaction conditions or catalyst preparations.

Generally, supported palladium catalysts, such as palladium on carbon and palladium on alumina, have been widely used for synthetic hydrogenations because of their high activities and selectivities.[7] However, supported catalyst variations have different features, especially regarding their adjustment in alkalinity.[5] Usually, these catalysts often contain considerable amounts of alkaline impurities, which may greatly influence the nature of the catalysts. In this work we carried out the hydrogenation of *p*-cresol with commercial palladium on carbon (Pd–C), water-washed Pd–C (Pd–C–N), acid-treated Pd–C (Pd–C–A), and base-treated Pd–C (Pd–C–B) as catalysts at varying hydrogen pressures in order to study the effects of the nature of the catalysts and the hydrogen pressure on the formation of the methylcyclohexanone intermediate. By simulating the varying composition of reaction mixtures vs. the reaction time by a computer program, the rate of hydrogenation and the selectivity for the methylcyclohexanone intermediate have been evaluated quantitatively as a function of the hydrogen pressure. The effects of alkaline substances contaminated in the catalysts on the relative reactivity of the intermediate ketone to the cresol and on the maximum yield of the ketone intermediate have also been evaluated.

Experimental

Materials. *p*-Cresol (Wako Pure Chemical Industries) was purified by treating with Raney nickel at 50—60 °C for 3 h to remove any catalyst poisons. 4-methylcyclohexanone (Wako Pure Chemical Industries) was dried over anhydrous $MgSO_4$ and then distilled before use.

Catalysts. Palladium on Carbon (Pd-C): Palladium on carbon, used as a standard catalyst (5 wt% Pd), was obtained from N.E.Chemcat Co.,Ltd.

Water-Washed Pd-C (Pd-C-N): The Pd–C catalyst (1.5 g) was gently washed in several portions with 2000 ml of water after pretreatment with H_2 in 100 ml of water for 2 h under atmospheric pressure at 25 °C.

Acid-Treated Pd-C (Pd-C-A): The Pd–C catalyst (3.0 g) was treated with 100 ml of a 0.1 mol dm^{-3} HCl solution in order to remove any alkaline impurities under atmospheric pressure of hydrogen at 25 °C for 40 min. After removal of the solution by vacuum filtration, the catalyst was then washed several times with a total of 2000 ml of water.

Base-Treated Pd-C (Pd-C-B): The Pd–C–N catalyst (1.5 g) was soaked in 100 ml of 0.22 mol $\mathrm{dm^{-3}}$ NaOH solution at 25 °C for 1 h. The catalyst was then washed with 1000 ml of water.

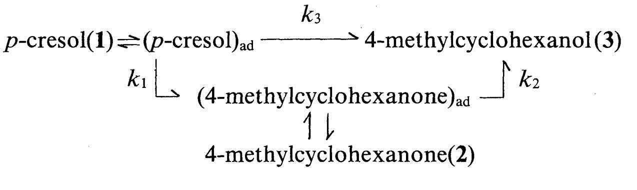
The catalysts thus prepared were all dried in vacuum over silica gel.

Solvent. Cyclohexane and methylcyclohexane (Wako Pure Chemical Industries) were distilled with the addition of a small amount of sodium, and then stored in a refrigerator.

Hydrogenation. All hydrogenations were performed in a 200 ml stainless-steel autoclave with a magnetically-driven stirrer. The autoclave was immersed in an oil bath maintained at 80 °C during hydrogenation. Cyclohexane (40 ml) (methylcyclohexane in the hydrogenations under 0.15 MPa) was used as the solvent. The catalyst (0.30 g) was pretreated in the solvent with 10 MPa of hydrogen at 80 °C for 30 min. After the pretreatment, 1.20 ml of the substrate was added into the mixture. The reaction mixutre was stirred at 80 °C under varying hydrogen pressure of 0.15—8.0 MPa. The stirrer was driven at 1000 rpm. Small portions of the reaction mixture were removed with a syringe, or through a tube at appropriate intervals.

Analysis of the Reaction Mixture. The reaction mixture was directly subjected to GLC using a fused silica capillary column of SUPELCOWAX$^{\mathrm{TM}}$10 (30 m, 0.53 mm ID, 1.0 μm film thickness) at 100—200 °C programmed at 4 °C $\mathrm{min^{-1}}$ with 5 ml $\mathrm{min^{-1}}$ nitrogen. The retention times were 6.6 min (4-methylcyclohexanone), 7.7 min (*cis*-4-methylcyclohexanol), 8.0 min (*trans*-4-methylcyclohexanol), and 21.5 min (p-cresol).

Kinetic Modelling. The Kinetics of the liquid-phase hydrogenation of phenolic compounds over palladium catalyst can be described by a Langmuir–Hinshelwood model with a non-competitive adsorption of hydrogen and the substrate, as proposed by Zwicky and Gut.[8,9] In general, the hydrogenation pathways for phenols can be expressed according to the following two routes: A direct route leading to cyclohexanols not via cyclohexanones and a consecutive route via cyclohexanone as the intermediate (see Scheme 1).[10] Therefore, Eqs. 1—3 were applied to the respective hydrogenation route in our present work. In these equations, m, k_i, b_i, and C_i represent the amount of catalyst, the rate constant for each hydrogenation route, the adsorption coefficient, and the concentration of each compound. The subscript numbers 1, 2, and 3 correspond to p-cresol, 4-methylcyclohexanone, and 4-methylcyclohexanol, respectively. First, k_2 and b_3/b_2 were evaluated from the hydrogenation of 4-methylcyclohexanone. Subsequently, k_1, k_3, b_2/b_1, and b_3/b_1 were determined by simulating the composition of the reaction mixture vs. the reaction time to fit the experimental data, using a computer program based on the Runge–Kutta–Gill routine.



Scheme 1. Hydrogenation routes of p-cresol.

$$-\frac{\mathrm{d}C_1}{\mathrm{d}t}=\frac{m(k_1+k_3)b_1C_1}{b_1C_1+b_2C_2+b_3C_3} \tag{1}$$

$$\frac{\mathrm{d}C_2}{\mathrm{d}t}=\frac{m(k_1b_1C_1-k_2b_2C_2)}{b_1C_1+b_2C_2+b_3C_3} \tag{2}$$

$$\frac{\mathrm{d}C_3}{\mathrm{d}t}=\frac{m(k_2b_2C_2+k_3b_1C_1)}{b_1C_1+b_2C_2+b_3C_3} \tag{3}$$

Analysis of the Sodium in the Catalysts. The catalyst (10 mg) was treated with 6.7 ml of a 0.05 mol $\mathrm{dm^{-3}}$ HCl solution for 20 min with stirring under atmospheric pressure of hydrogen at 25 °C. After removing the catalyst, the filtrate was diluted with water and subjected to a flame atomic absorption analysis with a sodium lamp (Shimazu AA630).

Results and Discussion

Figures 1 and 2 show diagrams for product distributions vs. the reaction time in typical hydrogenations of p-cresol over Pd–C and Pd–C–A catalysts, respectively, under 0.15 (a) or 5.0 (b) MPa of hydrogen pressure at 80 °C. The diagrams obtained with Pd–C–B and Pd–C–N were very similar to those with Pd–C and Pd–C–A, respectively. In all cases, hydrogenolysis to give methylcyclohexane did not occur. A hydrogen transfer reaction to form the ketone from methylcyclohexanol and cresol was not considered, since no cyclohexanone formation was found under these reaction conditions when a small portion of cyclohexanol was added to the reaction mixture. In contrast to the cases with Pd–C and Pd–C–B catalysts, three products other than the alcohol were formed over Pd–C–N and Pd–C–A catalysts after the cresol had been completely consumed. They appeared to be the ethers derived from a hydrogenative condensation of the ketone and the alcohol. These diagrams show that the Langmuir–Hinshelwood model is satisfactorily in accord with the experimental results throughout the course of the reaction.

Selectivity for the Formation of the Ketone Intermediates (*f*). Table 1 summarizes the selectivity (*f*), as defined by $k_1/(k_1+k_3)$, as well as the maximum yields in the formation of the ketone intermediate over various Pd–C catalysts. These values have been determined by a simulation based on the experimental results, as can be seen in Figs. 1 and 2. It is noteworthy that Pd–C and Pd–C–B catalysts, which contained considerable amounts of sodium (see Table 2), gave a high selectivity of 1.0 under 0.15 MPa hydrogen pressure. This result indicates that all of the cresol was hydrogenated via the ketone as the only intermediate and at the same time that an adsorption–desorption equilibrium with respect to the intermediate was established during the course of hydrogenation. The values of *f* on Pd–C–N and Pd–C–A were always smaller than 1.0

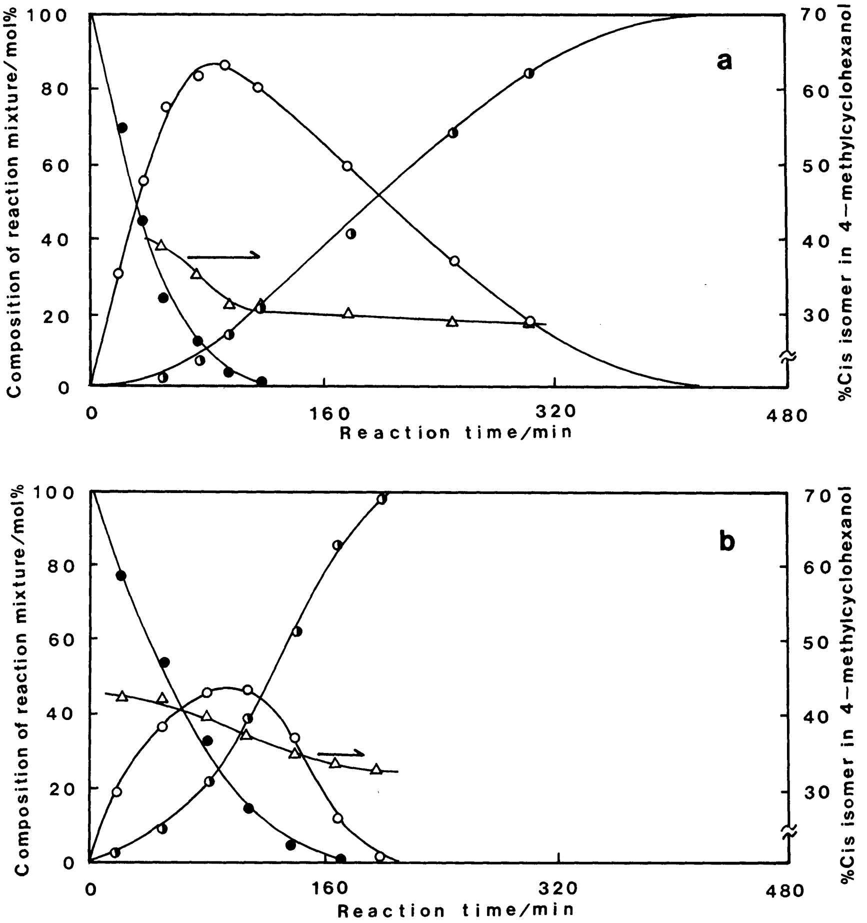


Fig. 1. Hydrogenation of *p*-cresol over Pd–C. The points are experimental values and the curves show the simulations in the composition of reaction mixture using the values given in Table 3. ●: *p*-cresol, ○: 4-methylcyclohexanone, ◑: 4-methylcyclohexanol, ⦶: bis(4-methylcyclohexyl)ether, △: %cis isomer in 4-methylcyclohexanol. **a**: Hydrogenation at 0.15 MPa and 80 °C in methylcyclohexane. **b**: Hydrogenation at 5.0 MPa and 80 °C in cyclohexane.

Table 1. Selectivity and Maximum Yield of the Ketone Intermediate in the Hydrogenation of *p*-Cresol

Catalyst	H_2 press / MPa	Selectivity f[a]	Maximum yield of ketone (%)[b]
Pd-C	0.15	1.0	85.9
Pd-C	1.0	0.91	64.5
Pd-C	5.0	0.92	47.6
Pd-C	8.0	0.89	41.0
Pd-C-N	0.15	0.95	85.3
Pd-C-N	5.0	0.91	52.1
Pd-C-A	0.15	0.94	88.4
Pd-C-A	1.0	0.91	78.0
Pd-C-A	5.0	0.86	67.0
Pd-C-A	8.0	0.85	62.4
Pd-C-B	0.15	1.0	79.4
Pd-C-B	5.0	0.86	53.7

a) Selectivity $f=k_1/(k_1+k_3)$. b) Evaluated values obtained by Eqs. 1—3.

Table 2. Sodium Content in Various Catalysts

Catalyst	Na content in catalyst/wt%
Pd-C	1.1
Pd-C-N	0.13
Pd-C-A	0.05
Pd-C-B	0.85

under all of the reaction conditions employed. Over all the catalysts, the selectivity, as well as the maximum yields of the ketone, decreased with increasing hydrogen pressure (compare Figs. 1a and 2a with Figs. 1b and 2b). The maximum yield of the ketone intermediate (88.4%) was obtained in hydrogenation over Pd–C–A at 0.15 MPa.

Relative Reactivity of the Ketone to the Cresol (*K*). The relative reactivity of the ketone to the cresol (*K*), defined by $k_2/(k_1+k_3)\times b_2/b_1$,[11] was also calculated by

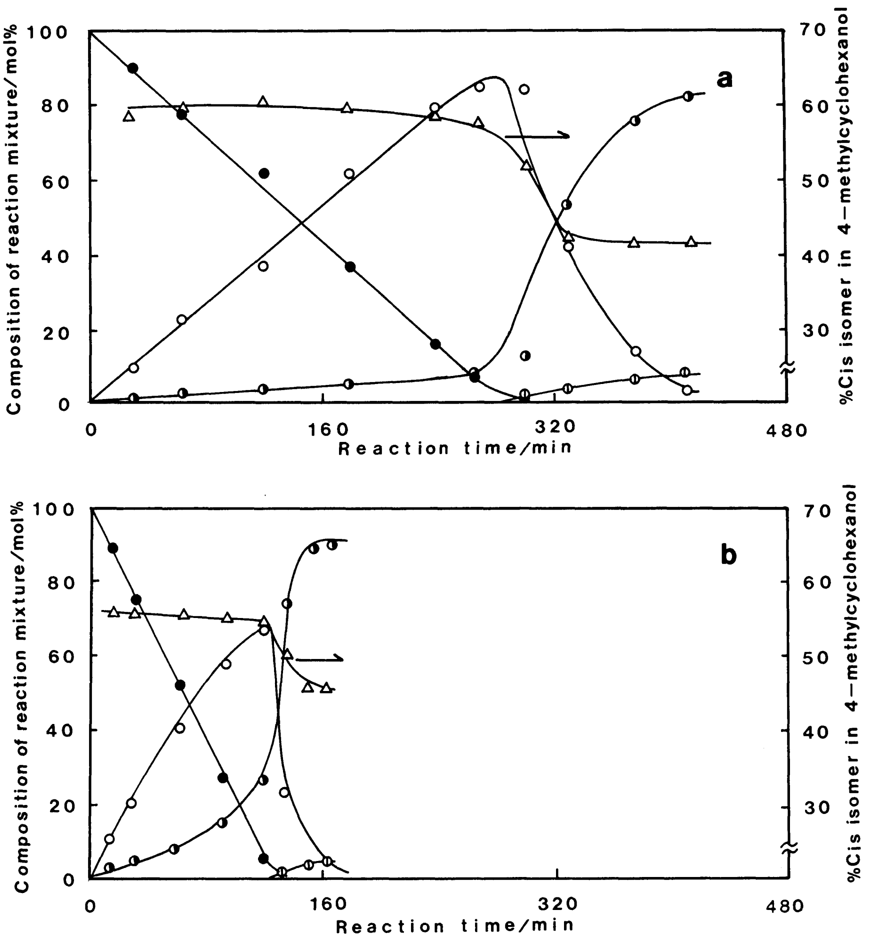


Fig. 2. Hydrogenation of *p*-cresol over Pd–C–A. For indications, see the footnotes in Fig. 1.

Table 3. Relative Reactivity of 4-Methylcyclohexanone to *p*-Cresol *K* and Related Data over Various Palladium Catalysts

Catalyst	H_2 press	$K^{a)}$	k_1+k_3	k_2	$k_2/(k_1+k_3)$	b_2/b_1	b_3/b_1
	MPa		$\times10^3$ mol min^{-1} (g-Pd)$^{-1}$				
Pd–C	0.15	0.047	12.1	2.87	0.24	0.20	0.016
Pd–C	1.0	0.156	8.31	6.80	0.82	0.19	0.015
Pd–C	5.0	0.46	7.78	9.44	1.21	0.38	0.045
Pd–C	8.0	0.62	8.47	10.58	1.25	0.50	0.090
Pd–C–N	0.15	0.026	2.87	6.76	2.36	0.011	0.0018
Pd–C–N	5.0	0.32	4.39	83.1	18.9	0.018	0.019
Pd–C-A	0.15	0.014	2.68	9.52	3.55	0.004	0.002
Pd–C–A	1.0	0.048	5.29	52.9	10.0	0.005	0.003
Pd–C–A	5.0	0.093	5.97	92.2	15.4	0.006	0.006
Pd–C–A	8.0	0.128	6.15	98.2	15.97	0.008	0.007
Pd–C-B	0.15	0.082	5.29	2.27	0.43	0.19	0.0086
Pd–C–B	5.0	0.26	4.38	5.67	1.29	0.20	0.0080

a) $K=k_2/(k_1+k_3)\times b_2/b_1$.

simulation. As shown in Table 3, the values of K depend greatly on the hydrogen pressure, and become very small at low hydrogen pressures, irrespective of the catalysts. A plot of log K as a function of log P_{H_2} is linear with slopes of 0.65 and 0.56 over Pd–C and Pd–C–A, respectively (see Fig.3). It is also noted that the values of K with Pd–C–A and Pd–C–N are always smaller than the corresponding values with Pd–C and Pd–C–B. Since the adsorption coefficients of *p*-cresol are 56—250 times larger than those of the ketone over Pd–C–N and Pd–C–A (see the values of b_2/b_1 in Table 3), it seems reasonable to consider that an adsorption–desorption equilibrium of the ketone during the course of hydrogenation was also established with these catalysts. Since the values of f over these catalysts were always less than unity (see Table 1), a route to give the alcohol not via the ketone intermediate is indicated to exist over these neutral or acidic catalysts. The stereochemistry of alcohol formation is also in line with the above-mentioned results. The values of the %cis isomer in 4-methylcyclohexanol gradually decreases over both Pd–C (see Fig.1) and Pd–C–B in the course of hydrogenation, while they are almost constant over both Pd–C–A (see Fig. 2) and Pd–C–N until the cresol completely disappears, and then decrease quickly by extents of about 20%. The values of the %cis isomer at the final stages were close to those obtained in the hydrogenation of 4-methylcyclohexanone.

The Hydrogenation Rate Constants of the Cresol and the Ketone (k_1+k_3 and k_2). The hydrogenation rate constants for the cresol and the ketone are shown in Table 3. The Pd–C catalyst was the most active for the hydrogenation of cresol, while Pd–C–A and Pd–C–N catalysts showed much greater activities for ketone hydrogenation than did Pd–C and Pd–C–B. Accordingly, the values of $k_2/(k_1+k_3)$ become rather large over Pd–C–A and Pd–C–N and, thus, the small values of K over these catalysts cannot be accounted for by these kinetic factors. The effect of the hydrogen pressure on the rate constants (k_1+k_3 and k_2) are also given in Table 3. The results show that k_2 increases with increasing hydrogen pressure over all the catalysts used, while k_1+k_3 is almost independent of the hydrogen pressure over Pd–C and Pd–C–B ; this, however, is not the case with Pd–C–A and Pd–C–N, although the effect of the hydrogen pressure on k_1+k_3 is much smaller than on k_2. A plot of log k_2 as a function of log P_{H_2} is almost linear with slopes of 0.45 and 0.90 over Pd–C and Pd–C–A, respectively, at the pressures lower than 1.0 MPa.

Regarding the great difference in the hydrogen pressure dependence of the rate constant between the cresol and the ketone, it is suggested that species of the active hydrogen on Pd responsible for the hydrogenation of *p*-cresol differ from those which are responsible for the hydrogenation of the ketone. The former hydrogen is supposed to be saturated on the surface of Pd, even under a very low hydrogen pressure. Suzuki et al. have reported that at least three species of activated hydrogen may exist over Pd–C catalyst.[12] These are weakly adsorbed hydrogen, dissolved hydrogen, and strongly adsorbed hydrogen, the relative existence ratio of which depends on the hydrogen pressure. Recently, it has also been observed that although a large amount of the hydrogen contained in a Raney nickel catalyst plays an important role in the hydrogenation of cyclohexanone, but this is not true for that of benzene.[13]

The Ratios of the Adsorption Coefficients of the Cresol and the Ketone (b_2/b_1). The values of b_2/b_1 were always smaller than 1.0 for all of the catalysts and reaction conditions. Especially, over the acidic Pd–C–A catalyst, b_2 was about 100 times smaller than b_1. This situation can be clearly seen in Fig. 2, where the hydrogenation of the ketone intermediate practically does not occur in the presence of the cresol ; it abruptly starts at the time when the cresol has been completely consumed, notwithstanding the fact that the rate constant for the ketone is much greater than that for the cresol over the acidic catalyst. Such a tendency was not obserbed over basic Pd–C and Pd–C–B catalysts, as can be seen in Fig.1.

The strength of adsorption of the cresol and the ketone may be influenced by the acidic or basic nature of the palladium catalysts. Therefore, competitive hydrogenations of the ketone and the cresol against toluene were investigated over Pd–C and Pd–C–A as catalysts, since the strength of adsorption would be less influenced with toluene than with *p*-cresol. The ratios of the adsorption coefficients of the ketone to toluene(b_2/b_T) as well as that of the cresol to toluene (b_1/b_T) have been determined, where b_T represents the adsorption coefficient of toluene. The values of b_2/b_T and b_1/b_T thus obtained were 1.05 and 1.98 over Pd–C under 5.0 MPa of hydrogen at 80 °C, while the corresponding values over Pd–C–A were 0.017 and 2.74.[14] The values of b_2/b_1 could be calculated by using the relationship $b_2/b_1 = b_2/b_T \times b_T/b_1$ to be 0.53 for Pd–C and 0.0062 for Pd–C–A, respectively. These values are in fairly good accordance with the values of 0.38 for Pd–C and 0.006 for Pd–C–A shown in Table 2. The hydrogenation rate of toluene was found to be only about 5 times larger over Pd–C–A than over Pd–C. If we assume that the strength of the adsorption of toluene does not greatly differ with basic and acidic catalysts, the very small value of b_2/b_T on Pd–C–A is considered to be a result that the adsorption of the ketone is very weak on the acidic catalyst. The much larger value of b_2/b_T with Pd–C may be associated with an alkaline impurity contained in the catalyst, which functions to greatly enhance the strength of adsorption of the ketone. Therefore, over Pd–C, the small values of K at low prssures depend not only on b_2/b_1, but also on $k_2/(k_1+k_3)$, in contrast to the cases with Pd–C–A.

It is to be noted that the values of b_2/b_1 do not vary much with the hydrogen pressure. Since the rate constant of hydrogenation of the cresol k_1+k_3 is also not

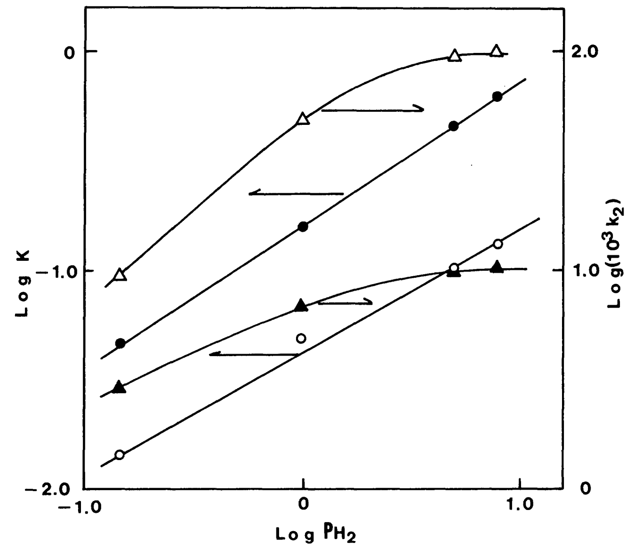
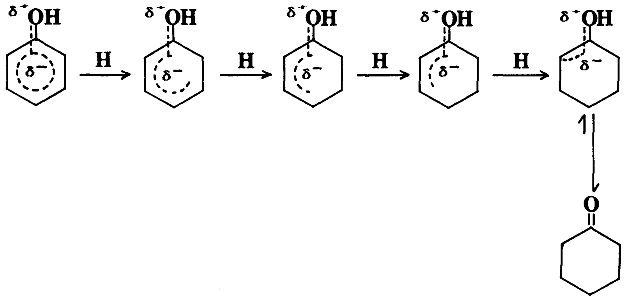


Fig. 3. Effect of hydrogen pressure on the relative reactivity of 4-methylcyclohexanone to *p*-cresol K and on the rate constant k_2. ●, ▲: Pd–C; ○, △: Pd–C–A.

greatly influenced by the hydrogen pressure, it is concluded that the great change in the values of K with the hydrogen pressure is caused by the sensitively varying rate constant of the ketone k_2, especially at pressures lower than 1.0 MPa (see Fig. 3). At pressures higher than 1.0 MPa, the values of b_2/b_1 appear to increase slightly with increasing hydrogen pressure. Since the values of b_3/b_1 also increase with increasing hydrogen pressure as shown in Table 3, the increase in the values of b_2/b_1 and b_3/b_1 appears to be caused by a decrease in the strength of the adsorption of *p*-cresol (b_1) at high hydrogen pressures.

The Hydrogenation Pathways of the Cresol over Palladium Catalyst. All of the palladium catalysts showed high selectivities of 0.81—1.0 for formation of the ketone intermediate, as shown in Table 1. Especially, the quantitative formation of the ketone as indicated by the value of 1.0, was obtained with basic Pd–C and Pd–C–B catalysts at 0.15 MPa. It was reported that the rhodium catalyst gave selectivities of 0.52—0.55 for the ketone intermediate in the hydrogenation of isomeric cresols.[15] The selectivity with the rhodium catalyst has been explained by the assumption that a random addition of hydrogen occurs over rhodium during the porocess to give various dihydro intermediates. For explaining the much more selective formation of the ketone intermediate over palladium, it is required that a regioselective addition of hydrogen to phenols should occur. If such a regioselective addition occurs in such a way as to maintain the resonance energy as much as possible in the processes to produce a series of the hydrogenation intermediates, the quantitative formation of the ketone can be easily explained, as shown in Scheme 2.[16] Since part of the cresol is presumed to be hydrogenated in form of phenoxide ion over catalysts containing alkaline impurities, the resonance-energy effect may play a greater role over basic Pd–C and Pd–C–B catalysts, resulting in a greater quantitative formation of the ketone intermediates over these catalysts. It is suggested that such a characteristic feature of palladium catalysts, as observed in the hydrogenation of phenols, results from a rather weak adsorption of phenols over palladium, since differences in the resonance stabilization energy between the transition states leading to various possible intermediates may play significant roles in determining such intermediates under a weak adsorption energy, as with palladium catalysts. Over Pd–C–A part of *p*-cresol is not hydrogenated via the ketone as an intermediate. This may be accounted for either by a decrease in the contribution of the phenoxide ion structure or by an increase in the strength of adsorption of the cresol over an acidic catalyst, which may depress the relative contribution of the resonance effect, and increase the hydrogenation routes not via the ketone intermediate, as in the hydrogenation over rhodium catalyst.



Scheme 2. Hydrogenation pathways of phenol leading to the quantitative formation of cyclohexanone intermediate over palladium catalyst.

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