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Effects of Alcoholic Solvents on the Formation of Cyclohexanones in the Hydrogenation of Phenols over Pd-C Catalysts[1)]

Michio HIGASHIJIMA and Shigeo NISHIMURA*
Department of Applied Chemistry, Tokyo University of Agriculture and Technology,
Koganei, Tokyo 184

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The catalytic hydrogenation of phenol and cresols (methylphenols) with commercial Pd on active carbon (Pd–C) and acid-treated Pd–C (Pd–C–A) has been studied kinetically in *t*-pentyl alcohol (*t*-PeOH) and cyclohexane as solvents under 5.0 MPa hydrogen pressure at 120 °C. With both of the catalysts the maximum yields of the cyclohexanone intermediates as well as the hydrogenation rates of the phenols decreased markedly in *t*-PeOH, compared with hydrogenation in cyclohexane. With Pd–C–A in *t*-PeOH the decrease in the yields of cyclohexanone intermediates was shown to be due only to the increase in the relative reactivity of the cyclohexanones to phenols (K). On the other hand, with Pd–C the marked decreases were attributed not only to the increases in the values of K but also to the decreases in the selectivity for the formation of the ketone intermediates (f). The rates decreased in the order phenol>*m*->*p*->*o*-cresol, irrespective of the catalysts and solvents. The relative reactivities and strengths of the adsorption of phenol to isomeric cresols were evaluated by both individual and competitive hydrogenation. It is suggested that the phenols are adsorbed on the catalysts both at the benzene nucleus and the hydroxyl group, and that the remarkable effects of alcoholic solvents over basic Pd–C result from the interaction of the hydroxyl groups as phenoxide ions with alcoholic solvents which may weaken adsorption at the phenoxide ions.

In a preceding paper[1)] it was shown that the formation of the cyclohexanone intermediate in the palladium-catalyzed hydrogenation of *p*-cresol (4-methylphenol) depends greatly on the catalysts and reaction conditions employed. Both the alkaline impurities associated with catalyst preparations and the hydrogen pressure are the most important factors which affect the selectivity for the formation of the ketone intermediate as well as the relative reactivity of the ketone to the cresol. The nature of the solvents employed has also been found to have significant effects on the formation and the relative reactivity of the ketone intermediate. The effects of solvents depend on the nature of the catalysts as well as the structure of the phenolic compounds hydrogenated. In this study we carried out the hydrogenation of phenol and isomeric cresols in cyclohexane and *t*-pentyl alcohol (*t*-PeOH) as solvents with a commercial palladium on carbon (Pd–C) and acid-treated Pd–C (Pd–C–A) as catalysts. Hydrogenation in both the solvents was compared on the basis of the evaluated kinetic parameters. The effects of the alcoholic solvent, which differ on Pd–C and Pd–C–A, are also discussed.

Experimental

Materials. All of the phenols and solvents were commercial products purified by treating with Raney nickel at 50—60 °C for 3 h to remove any catalyst poisons. Isomeric methylcyclohexanones (Wako Pure Chemical Industries) were dried over anhydrous $MgSO_4$ and then distilled before use.

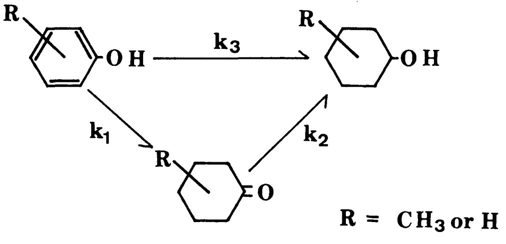
Catalysts. Palladium on Carbon (Pd-C): The palladium on carbon used as a standard catalyst (5 wt% Pd) was obtained from N. E. Chemcat Co., Ltd. The sodium content in the catalyst was ca. 1 wt%, as determined by a flame atomic absorption analysis.

Acid-Treated Pd-C (Pd-C-A): The Pd–C catalyst (3.0 g) was treated with a 100 ml of 0.1 M (1 M=1 mol dm^{-3}) HCl solution in order to remove any alkaline impurities under atmospheric pressure of hydrogen at 25 °C for 40 min. The catalysts were separated from the solution by vacuum filtration and then washed several times with a total of 2000 ml of hot distilled water. By these treatments the sodium content in the catalyst was decreased to less than 0.05 wt%.

Hydrogenation. After pretreatment of the catalyst with 10 MPa of hydrogen at 120 °C for 40 min, phenols (0.10—40.0 ml) were hydrogenated with the catalyst (0.10—0.40 g) in a solvent (or without solvent) at 120 °C under a hydrogen pressure of 5.0 MPa in a 200 ml stainless-steel autoclave with a magnetically-driven stirrer. The total volume of the reaction mixture was always adjusted to 40 ml. The stirrer was driven at 1000 rpm. Under these conditions any diffusion of the materials appeared to be unrelated to a rate-determining step. In hydrogenation without a solvent, the solvent was carefully removed by a syringe after the catalyst (0.40 g) had been pretreated in cyclohexane (20 ml) with 10 MPa of hydrogen at 120 °C for 40 min.

The reaction mixture was directly subjected to GLC using a fused silica capillary column of SUPELCOWAX™10 (30 m, 0.53 mm ID, 1.0 μm film thickness).

Kinetic Modelling. Except for hydrogenation over Pd–C in alcoholic solvents, a Langmuir–Hinshelwood model (described by Zwicky and Gut[2,3)]) was applied in order to simulate the reaction, while assuming the establishment of an adsorption–desorption equilibrium of the ketone intermediate during the course of the hydrogenation. The hydrogenation routes of phenols over Pd–C catalysts are described in Scheme 1. According to this scheme, Eqs. 1—3 were applied to the respective hydrogenation route. In these equations, k_i, b_i, and C_i represent the rate for each hydrogenation route, the adsorption coefficient, and the concentration of each compound, respectively. Subscripts 1, 2, and 3 refer to the phenols, cyclohexanones, and cyclohexanols, respectively. First, k_2 and b_3/b_2 were evaluated based on the hydrogenation of the cyclohexanones. Subsequently, k_1, k_3, b_2/b_1, and b_3/b_1



Scheme 1. Hydrogenation routes of phenols over Pd–C.

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.

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

$$\frac{\mathrm{d}C_2}{\mathrm{d}t}=\frac{k_1b_1C_1-k_2b_2C_2}{1+b_1C_1+b_2C_2+b_3C_3} \tag{2}$$

$$\frac{\mathrm{d}C_3}{\mathrm{d}t}=\frac{k_2b_2C_2+k_3b_1C_1}{1+b_1C_1+b_2C_2+b_3C_3} \tag{3}$$

In hydrogenation over Pd–C in *t*-PeOH it is not certain whether the adsorption–desorption equiliblium of the ketone intermediate was attained. Therefore, Eq. 4[4] was applied in order to estimate the selectivity for the cyclohexanones desorbed from the catalyst surface (f) and a constant related to the relative reactivity of cyclohexanones to phenols (K):

$$C_2=\frac{f}{K-1}(C_1-C_1{}^K) \tag{4}$$

Results and Discussion

Hydrogenation of *p*-Cresol over Pd–C in Various Alcoholic Solvents. The effects of various solvents on the maximum yields of the 4-methylcyclohexanone intermediate and on the hydrogenation rate of *p*-cresol (k_1+k_3) are listed in Table 1 regarding hydrogenation over Pd–C at 120 °C and 5.0 MPa of hydrogen. It can be seen that the maximum yields of the ketone as well as k_1+k_3 greatly decreased in all of the alcoholic solvents, compared to those in nonpolar cyclohexane and decalin. Great effects were observed even in tertiary alcohols, such as *t*-BuOH and *t*-PeOH.

Selectivity for the Formation of the Ketone Intermediates (f). In Tables 2 and 3, the results obtained with Pd–C and Pd–C–A catalysts, respectively, in *t*-PeOH and in cyclohexane are given with respect to the selectivity (f), as defined by $k_1/(k_1+k_3)$, the maximum yields, and related kinetic data in the formation of the ketone intermediate. These values were evaluated either from Eqs. 1—3 by computer simulation, as described in a preceding paper,[1] or from Eq. 4 based on the experimental results given in Fig. 1.

The values of f are functions of the concentration of the phenols in alcoholic solvents (Fig. 2 for *p*-cresol). The decrease in the values of f with decreasing concentration was greater over Pd–C than over Pd–C–A. When the concentration of phenols in *t*-PeOH was 6.25 mol%, the

Table 1. Hydrogenation of *p*-Cresol in Various Solvents over Pd–C Catalyst[a]

Solvent	Max yield of the ketone %	Hydrogenation rate (k_1+k_3) $\times10^3$ mol min^{-1} (g-Pd)$^{-1}$
None[b]	40.2	126.6
Cyclohexane	76.7	78.4
Decalin	66.8	129.1
t-Pentyl alcohol	19.4	10.3
t-Butyl alcohol	29.8	9.7
s-Butyl alcohol	14.4	12.5
Isobutyl alcohol	23.1	9.5
Butyl alcohol	14.8	6.3
Isopropyl alcohol	11.1	8.3

a) *p*-Cresol (2.50 ml) was hydrogenated in 38 ml of solvent with 0.40 g of 5% Pd–C at 120 °C under 5.0 MPa of hydrogen. b) *p*-Cresol (40 ml) was hydrogenated without solvent under the same condition as described above.

Table 2. Kinetic Data Concerning the Hydrogenation of Phenols with Pd–C Catalyst[a]

Phenol	Solvent	Max yield of the ketone	f[b]	K[c]	k_1+k_3	k_2	$k_2/(k_1+k_3)$	b_2/b_1
		%			$\times10^3$ mol min^{-1} (g-Pd)$^{-1}$			
Phenol	C_6H_{12}	78.0	0.98	0.084[d]	167.3	25.6	0.15	0.55
o-Cresol	C_6H_{12}	77.6	0.94	0.060[d]	36.3	10.9	0.30	0.20
m-Cresol	C_6H_{12}	84.2	0.97	0.044[d]	116.7	17.0	0.15	0.30
p-Cresol	C_6H_{12}	76.6	0.95	0.096[d]	78.4	24.9	0.32	0.30
Phenol	*t*-PeOH	41.8	0.73[e]	0.3[e]	19.7	37.8	1.92	—
o-Cresol	*t*-PeOH	35.2	0.86[e]	0.8[e]	6.8	17.7	2.59	—
m-Cresol	*t*-PeOH	22.1	0.60[e]	1.2[e]	12.4	39.0	3.14	—
p-Cresol	*t*-PeOH	20.0	0.60[e]	1.2[e]	10.3	34.2	3.33	—

a) The substrate (1.20—2.50 ml) was hydrogenated in 38 ml of solvent with 0.10—0.40 g of the catalyst at 120 °C under 5.0 MPa of hydrogen. b) Selectivity for the cyclohexanone intermediate given by $k_1/(k_1+k_3)$. c) Relative reactivity of the cyclohexanone to the phenol. d) The K values are given by $k_2/(k_1+k_3)\times b_2/b_1$. e) Evaluated from Eq. 4.

Table 3. Kinetic Data Concerning the Hydrogenation of Phenols with Pd–C–A Catalyst[a)]

Phenol	Solvent	Max yield of the ketone	f[b)]	K[b)]	k_1+k_3	k_2	k_4[c)]	$k_2/(k_1+k_3)$	b_2/b_1
		%			$\times 10^3$ mol min^{-1} (g-Pd)$^{-1}$				
Phenol	C_6H_{12}	75.2	0.91	0.049	77.3	318	59.2	4.11	0.012
o-Cresol	C_6H_{12}	74.2	0.91	0.071	27.4	487	3.1	17.80	0.004
m-Cresol	C_6H_{12}	85.4	0.92	0.020	69.4	136	30.0	1.96	0.010
p-Cresol	C_6H_{12}	75.1	0.88	0.048	68.2	363	48.3	5.32	0.009
Phenol	*t*-PeOH	62.0	0.93	0.20	51.2	64	1.3	1.33	0.150
o-Cresol	*t*-PeOH	62.5	0.90	0.17	19.2	110	0	5.73	0.030
m-Cresol	*t*-PeOH	63.1	0.93	0.19	44.1	126	1.4	2.86	0.070
p-Cresol	*t*-PeOH	50.4	0.89	0.35	28.3	123	1.5	4.33	0.080

a) For the reaction conditions, see footnote a) in Table 2. b) See footnotes b) and c) in Table 2. c) Formation rate of bis(alkylcyclohexyl) ether.

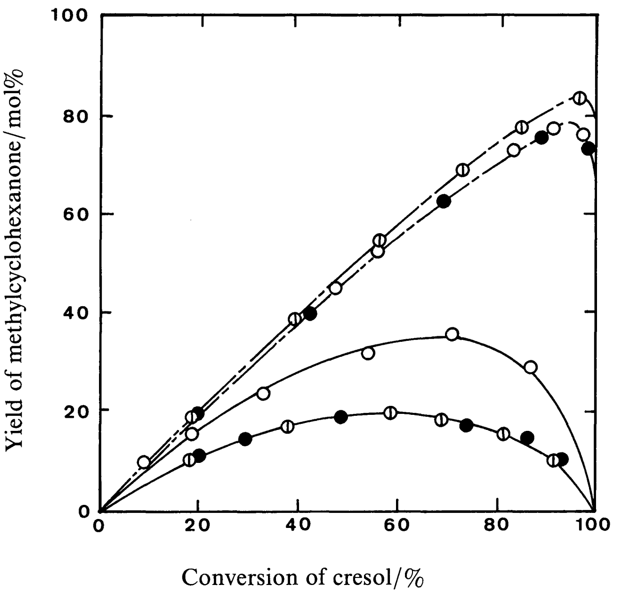


Fig. 1. Hydrogenation of isomeric cresols in cyclohexane (dotted lines) and in *t*-pentyl alcohol (full lines) with Pd–C at 120 °C and 5.0 MPa of hydrogen. ○: *o*-cresol, ⦶: *m*-cresol, ●: *p*-cresol. The points are experimental values. The full lines indicate the theoretical curves given by Eq. 4 for the hydrogenations in *t*-PeOH when f=0.86, K=0.8 for *o*-cresol and f=0.60, K=1.2 for *m*- and *p*-cresols. For the values of f and K in cyclohexane, see Table 2.

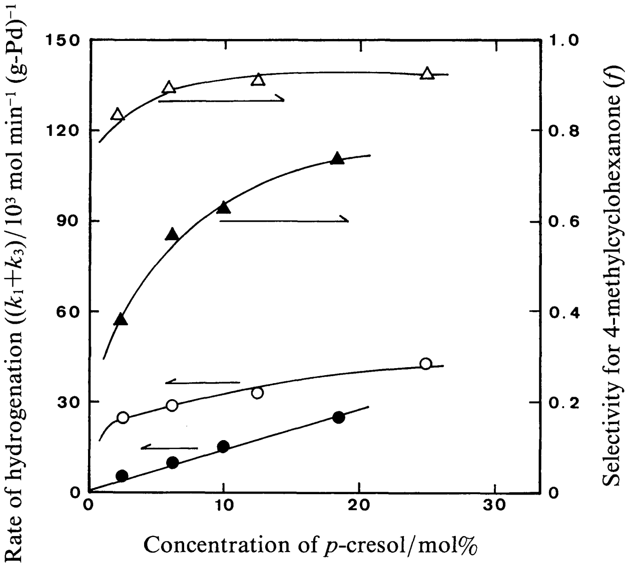


Fig. 2. Concentration dependences of the rate of hydrogenation of *p*-cresol and of the selectivity for 4-methylcyclohexanone in *t*-PeOH at 120 °C and 5.0 MPa of hydrogen. ●, ▲: Pd–C; ○, △: Pd–C–A.

values of f decreased to 0.73 for phenol, 0.86 for *o*-cresol, and 0.60 for *m*- and *p*-cresols over Pd–C, while those in cyclohexane were as high as 0.94—0.98. It is noted that the decrease in the value of f was smaller for *o*-cresol than for the other phenols. On the other hand, over Pd–C–A the values of f were comparable to those obtained in cyclohexane.

The hydrogenation of phenols over a Pd–C catalyst was reported to give the corresponding cyclohexanones selectively in consecutive hydrogenation pathways.[5)] The present study, however, shows that this was not the case for hydrogenation over basic Pd–C in an alcoholic solvent, and that the extent of such solvent effects depended on the nature of the catalysts as well as the structure of the substrates.

Relative Reactivity of the Ketones to the Phenols (K). The relative reactivity of the ketones to the phenols (K) was evaluated from Eqs. 1—3, where K is defined by $k_2/(k_1+k_3)\times b_2/b_1$, or from Eq. 4. When equilibrium of the adsorpton–desorption for the ketone intermediate is not established during hydrogenation of the phenols, K would represent $k_2/(k_1+k_3)\times k_a/b_1(k_d+k_2)$,[4)] where k_a and k_d refer to the adsoption and desorption rates on the catalyst surface of the ketone intermediate, respectively.

The values of K for Pd–C are 4—27 times larger in *t*-PeOH than in cyclohexane. Thus, rather small amounts of the ketone intermediate, which accumulated with Pd–C in *t*-PeOH, is concluded to be due not only to the decrease in the selectivety (f), but also to the large values of K in *t*-PeOH. These trends were not seen in hydrogenation with Pd–C–A, where the 12—25%

Table 4. Relative Hydrogenation Rates and Adsorption Coefficients of Phenols[a)]

Compound	Relative hydrogenation rate			Relative adsorption coefficient			pK_a
	Pd–C	Pd–C–A	(Pt)[b)]	Pd–C	Pd–C–A	(Pt)	
Phenol (toluene)	1	1	(1)	1	1	(1)	9.89
o-Cresol (*o*-xylene)	0.22	0.35	(0.619)	0.30	0.37	(0.478)	10.2
m-Cresol (*m*-xylene)	0.70	0.90	(0.857)	0.39	0.36	(0.294)	10.0
p-Cresol (*p*-xylene)	0.47	0.88	(1.075)	0.45	0.32	(0.246)	10.17

a) The data is evaluated by individual and competitive hydrogenations; equimolar amounts of two phenols (1.13 mmol for each phenol) were hydrogenated over 0.10 g catalyst under 5.0 MPa hydrogen at 120 °C in 40 ml cyclohexane. b) The data in parentheses are the results by Rader and Smith (Ref. 6). The hydrogenation was done with Adams platinum in AcOH under 0.2—0.4 MPa of hydrogen at 30 °C.

decrease in the maximum yields of the ketone in *t*-PeOH can be attributed only to the increases in the values of K, since the values of f did not differ between *t*-PeOH and cyclohexane.

Hydrogenation Rates for the Phenols and the Ketones (k_1+k_3 and k_2). The hydrogenation rates for the phenols (k_1+k_3) and the corresponding ketones (k_2) are also given in Tables 2 and 3. The activity of Pd–C for the hydrogenation of the phenols is rather low in *t*-PeOH, compared to its high activity in cyclohexane. Although in cyclohexane the hydrogenation rates were almost zero order in the concentration of phenols over Pd–C and Pd–C–A, the rates were nearly first order over Pd–C in relatively dilute solutions, as shown in Fig. 2 for the hydrogenation of *p*-cresol in *t*-PeOH. The rates over Pd–C–A, however, became zero order in *t*-PeOH at concentrations greater than ca. 20 mol% (Fig. 2). This indicates that in the alcohol *p*-cresol is adsorbed on Pd–C much more weakly than on Pd–C–A. It is suggested that the solvation of the alcohol around the phenoxide ion formed on the basic catalyst may play an important role to weaken adsorption at the phenoxide ion.

The hydrogenation rates always decreased in the order phenol>*m*->*p*->*o*-cresol, irrespective of the catalysts and solvents (Tables 2, 3, and 4). It is interesting to note that the order of the hydrogenation rate is parallel to the order of the pK_a values of these phenols. The differences in the rates among the phenols are considerable over Pd–C, while they are not great over Pd–C–A, except for *o*-cresol. These results suggest that the rate-determining step for hydrogenation over Pd–C is related to the stability of phenoxide ions which are formed on the basic catalyst.

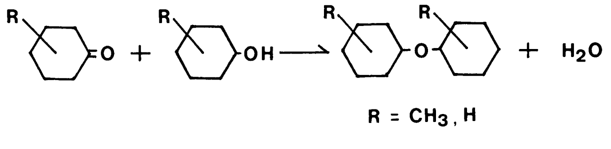
For ketone hydrogenation, especially in cyclohexane, Pd–C–A is much more active than is Pd–C. With Pd–C–A, except in the hydrogenation of *o*-cresol, a hydrogenative condensation of cyclohexanone and the alcohol to give dicyclohexyl ethers (see Scheme 2) became significant during the later stages of hydrogentation. The rates for this reaction are also included in Table 3, along with the hydrogenation rates of the ketones. Under these circumstances, however, the values of K as well as k_2 may be influenced by the ether formation reaction, and would thus be reliable only in limited extents. On the other hand, these ethers were detected only in trace amounts in *t*-PeOH. Interestingly, over Pd–C the values of k_2 were 1.4—2.3 times larger in *t*-PeOH than in cyclohexane, while those over Pd–C–A were smaller in *t*-PeOH than in cyclohexane.

The Ratios of the Adsorption Coefficients of the Phenols and the Ketones (b_2/b_1). As discussed in the preceding paper,[1)] on Pd–C–A the adsorption–desorption equilibrium of the intermediate ketone is considered to be established during hydrogenation in cyclohexane, although the values of f on Pd–C–A are always less than unity. A similar establishment of the adsorption–desorption equilibrium in *t*-PeOH can be reasonably assumed, since the f values over Pd–C–A did not differ between those in *t*-PeOH and those in cyclohexane, as mentioned above. Therefore, the simulation method was applied to an evaluation of the b_2/b_1 values. As shown in Table 3, the values of b_2/b_1 over Pd–C–A were always very small in *t*-PeOH, though they were ca. 10-times greater than those in cyclohexane.

Competitive Hydrogenation of the Phenols. In order to determine the relative strengths of adsorption for the phenols, competitive hydrogenation in equimolar mixtures of *p*- or *m*-cresol against *o*-cresol and of *m*-cresol against phenol were studied with Pd–C and Pd–C–A in cyclohexane. The relative reactivities ($K_{A,B}$) and the ratios of the adsorption coefficients (b_A/b_B) were calculated by employing the following relationship:[6)]

$$K_{A,B} = \log(C_{A,0}/C_A)/\log(C_{B,0}/C_B) = k_A b_A/k_B b_B,$$

where $K_{A,B}$ represents the relative reactivity of A to B, $C_{A,0}$ and $C_{B,0}$ are the initial concentrations of A and B, C_A and C_B are the concentrations of A and B at given reaction times and k_A and k_B are the rate constants for the individual hydrogenation of A and B, respectively. In all cases, satisfactory linear relationships between $\log(C_{A,0}/C_A)$ and $\log(C_{B,0}/C_B)$ were obtained; the values



Scheme 2. Hydrogenative condensation of cyclohexanones and cyclohexanols over Pd–C–A catalyst.

of K were determined from the slopes by a least-square method. The results are summarized in Table 4 along with the results by Rader and Smith concerning the competitive hydrogenation of toluene against isomeric xylenes over a platinum catalyst⁶⁾ for a comparison.

The orders in the relative adsorption coefficients, thus obtained, are: phenol>*p*->*m*->*o*-cresol over Pd–C and phenol>*o*->*m*->*p*-cresol over Pd–C–A. Since the strength of phenol adsorption is always greater than those of the cresols, it appears that the adsorption of cresols is weakened by a steric effect (rather than by an electronic effect) of the methyl group.

It was found that the order in the relative adsorption coefficients is the same for isomeric cresols over Pd–C–A and for isomeric xylenes over platinum. The strength of adsorption over Pd–C–A may therefore depend on the accessibility of the benzene nucleus to the catalyst surface, as postulated regarding the adsorption of polymethylbenzenes.⁶⁾ On the other hand, the results over Pd–C suggest that the relative strength of the adsorption of cresols depends on the relative position of the hydroxyl group to the methyl groups, since the strength of adsorption decreases with increasing degree of the steric interference of the methyl group to the hydroxyl group, probably in the state of phenoxide ions. It may thus be considered that the phenols on Pd–C are adsorbed both at the nucleus and the hydroxyl group. A slow hydrogenation of *o*-cresol over Pd–C supports the view that the adsorption of *o*-cresol is more strongly hindered in the state of the phenoxide ion formed on the basic catalyst.

Under the same conditions, phenol was hydrogenated far more readily than benzene over Pd–C. The hydrogenation rate was 10.5×10^{-3} mol min^{-1} (g-Pd)$^{-1}$ for benzene, compared to 167.3×10^{-3} for phenol. In contrast, over Pd–C–A the rates were 53.7×10^{-3} for benzene⁷⁾ and 76.0×10^{-3} for phenol. These facts also support the idea that the hydrogenation of phenol is greatly promoted by strong adsorption resulting from the phenoxide ion formed on the basic catalyst in nonpolar solvents. Such an adsorption at the phenoxide ions appears to be greatly hindered in alcohols, as mentioned before, probably due to solvation of the alcohols around the phenoxide ions. This consideration is supported by the result that the rate in *t*-PeOH, compared to that in cyclohexane, is decreased to the least extent in *o*-cresol among phenol and cresol isomers (see Table 2). Such solvation might be hindered to greatest extent by the methyl group located near the hydroxyl group in *o*-cresol.

The solvent effects on the reactivities of cyclohexanones is another factor which may affect the formation of intermediates. However, these solvent effects are not so pronounced with the ketones (see Tables 2 and 3), since phenols are adsorbed only weakly and hydrogenated rather slowly in alcohols over Pd–C, as discussed above. It is probable that in alcoholic solvents an adsorption–desorption equilibrium of the cyclohexanone intermediates is not fully established during the course of hydrogenation, resulting in smaller values of f and maximum yields compared to those in cyclohexane or over Pd–C–A.

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