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Selectivity of Group VIII Metals for the Catalytic Hydrogenation and Hydrogenolysis of Phenol

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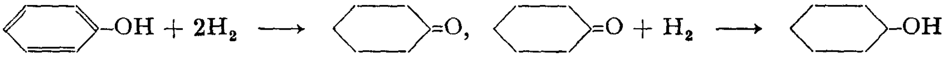
The hydrogenation of phenol has been investigated over group VIII metals by a gas chromatographic pulse technique. Major products were found to be cyclohexanone and cyclohexanol, but benzene, cyclohexane and other hydrocarbons were also formed.

The relative amount of cyclohexanol over cyclohexanone formed during the hydrogenation varied by a factor of about 100 depending on both catalyst and reaction temperature. This result was interpreted in terms of the relative catalytic activity of metals for the consecutive reaction:



The initial product due to the breaking of the carbon–oxygen bond was benzene rather than cyclohexane even when cyclohexanol or cyclohexanone was injected in the presence of hydrogen. This unusual result was briefly discussed.

Introduction

The catalytic hydrogenation of phenol has been investigated by many workers.[2] The activities of iridium, palladium, platinum, rhodium and ruthenium for the hydrogenation in liquid phase were reported by Rylander and Steele,[3] according to whom the rate of hydrogenation varied greatly with solvent, and the activities of these catalysts appeared to depend largely on experimental circumstances such as poisoning resistance, re–use and product composition rather than on initial activity.

It has been recognized that the catalytic hydrogenation of phenol produces not only cyclohexanol but also cyclohexanone, benzene and cyclohexane depending on both catalyst and reaction temperature. Thus, Jungers and Coussenant[4] proposed, studying the kinetics of the reaction on nickel in liquid phase, that cyclohexanone is an intermediate in the following consecutive reaction:

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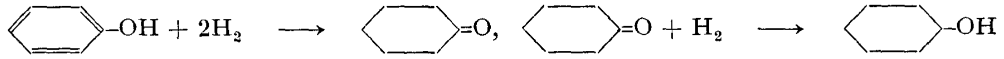
[1] Location: *Hongo, Bunkyo-ku, Tokyo.*

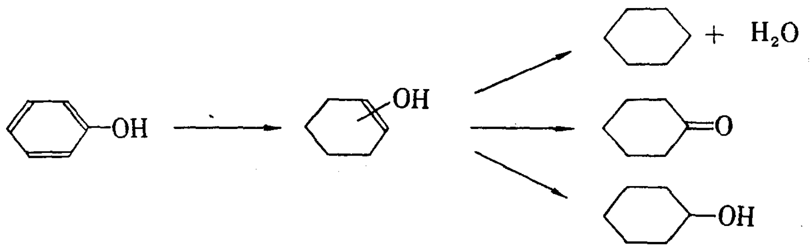
[2] H. A. Smith, "Catalysis," Vol. 5, Reinhold, New York, 1957, p. 175.

[3] P. N. Rylander and D. R. Steele, *Engelhard Ind. Tech. Bull.*, 3, 19 (1962).

[4] F. Coussenant and J. C. Jungers, *Bull. Soc. Chim. Belges*, 59, 295 (1950).



On the other hand, Smith and Stump⁵⁾ suggested, studying the same reaction on Adams' platinum as well as on rhodium catalyst in liquid phase, that cyclohexenol is an intermediate which is converted to cyclohexanol and cyclohexane.



These authors considered that cyclohexanone may be found in the product just because of its more thermodynamical stability for 1-cyclohexenol. The mechanism was suggested on the basis of the fact that the rate of hydrogen uptake is slower for cyclohexanone than for phenol on 5% rhodium-on-alumina catalyst. Unfortunately, it is not obvious whether or not the rate of hydrogen uptake for phenol observed by Smith and Stump represents the rate of formation of cyclohexanol.

In the foregoing several papers,⁶⁻⁹⁾ we have applied a gas chromatographic pulse technique to the study of the hydrogenation of cyclohexene, xylene and aniline on transition metals of group VIII. Reaction products and relative rates of formation were readily determined by this method, and hence it was possible to follow reaction pathways. In particular, the method proved to be useful to judge the hydrogenation selectivity of a series of catalysts under a certain experimental condition. Since the catalytic hydrogenation of phenol referred above was carried out under different reaction conditions and catalyst systems, and hence does not permit any correlation with each other, it would be worthwhile to investigate the hydrogenation of phenol in gas phase by the pulse technique and to discuss the conflicting views concerning the mechanism of the hydrogenation.

In the present paper we shall report the result of such works.

Experimental

Apparatus and Procedure——Shimadzu gas chromatograph of type GC-1B was used for the purpose. A stainless steel reactor tube (6 ϕmm), containing a given catalyst and surrounded by an electric furnace, was connected to a separation column containing PEG 6000 or DEGS coated celite (each 2.25 m long). The temperature of the reactor was maintained in the range from 170 to 300° and the separation column was kept usually at 150°. Hydrogen was used as the carrier, its flow rate being kept constant at 100 ml/min in most experiments. Usually, a sample of 3 μl phenol was injected into a stream of hydrogen to pass through the reactor tube, and the effect of catalyst and reaction temperature on the distribution of reaction products was measured.

Materials——All reagents were of guaranteed reagent grade. Phenol was supplied from Osaka Organic Chem. Co., and cyclohexanol, cyclohexanone, benzene and cyclohexane, which also served as reactants, were purchased from Tokyo Kasei Co. Gas chromatographic analysis of these reagents indicated that they are nearly 100% pure.

Nickel, cobalt and iron catalysts were prepared from their basic carbonates, and ruthenium, rhodium, palladium, iridium and platinum catalysts were prepared from their chlorides impregnated on silicon carbide

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5) H. A. Smith and B. L. Stump, *J. Am. Chem. Soc.*, **83**, 2739 (1961).
6) H. Yamamoto, M. O'hara and T. Kwan, *Chem. Pharm. Bull.* (Tokyo), **12**, 959 (1964).
7) H. Yamamoto, M. O'hara and T. Kwan, *Chem. Pharm. Bull.* (Tokyo), **13**, 724 (1965).
8) H. Yamamoto, K. Noda, H. Horiguchi and T. Kwan, *Chem. Pharm. Bull.* (Tokyo), **15**, 752 (1967).
9) H. Yamamoto, H. Horiguchi, K. Noda and T. Kwan, *Chem. Pharm. Bull.* (Tokyo), **15**, 1129 (1967).

having the surface area less than 1 m^2/g. All samples were reduced by hydrogen around 300° for five hours except iron which was reduced at 380° for forty hours. The amount of catalyst used was 0.4—0.6 g except iron (1.0 g). The content of metal in the supported catalyst was kept mostly to about 5 wt. %.

Result

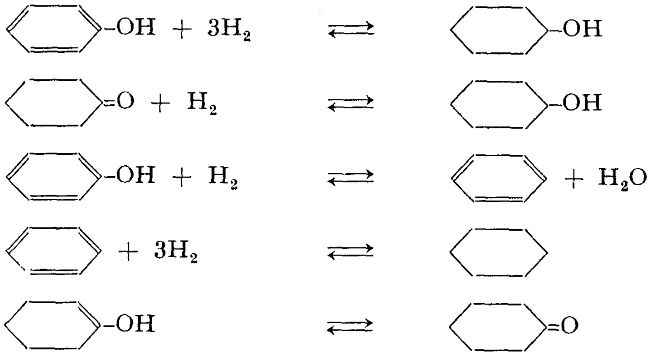
Thermodynamical Aspects of Related Reactions

The hydrogenation of aromatic compounds is exothermic; dehydrogenation dominates over hydrogenation with increasing reaction temperature. In view of possible hydrogenation-dehydrogenation reactions that would occur during the hydrogenation of phenol on metals, it would be pertinent to examine thermodynamical aspects of related reactions before the hydrogenation measurements.

In the previous paper[6] we have shown that the hydrogenation of benzene, injected as a pulse into hydrogen carrier, is readily equilibrated during passage through a reactor tube if a highly active catalyst such as platinum–alumina is employed. The ratio of cyclohexane to benzene leaving the catalyst layer was found to depend on the reaction temperature only; it was independent on the flow rate. On such basis, the equilibrium partial pressure for hydrogen has been estimated to be 0.5 atm in the reactor tube (inlet pressure: 1.5 atm).

Since the present experiment is being carried out under the same apparatus and experimental condition, it would be justified to presume the same partial pressure for hydrogen in the reactor.

Let us examine the equilibria of the following reactions:



(1)

(2)

(3)

(4)

(5)

Thermodynamical data were not sufficient to evaluate the equilibria as function of temperature except for hydrocarbons. Therefore, an approximate method[10] was employed to calculate the free energies of organic compounds in the range from 25 to 370°. We adopted two parameters due to Krevelen and Cherimin[11] to evaluate the free energies. These values were shown in Table I together with the thermodynamical quantities available in the handbook. In the light of these data, the equilibrium ratio of hydrogenated species to dehydrogenated one in the above reactions were calculated assuming that the partial pressure of hydrogen is constant at 0.5 atm. The results are shown in Fig. 1 against the reciprocal of the absolute temperature. The open circles show the ratio evaluated from the equilibrium constant observed by Brinbaum[12] which agree well with the calculated ones.

Fig. 1 shows, as expectedly, that hydrogenation or hydrogenolysis is generally favored at lower temperatures, and that the hydrogenolysis of phenol to produce benzene and water is thermodynamically feasible over the entire temperature range under investigations. We

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[10] G. J. Janz, "Estimation of Thermodynamical Properties of Organic Compounds," Academic Press Inc. Publishers, New York, 1958.

[11] D. W. Van Krevelen and H. A. G. Cherimin, *Chim. Eng. Sci.*, **1**, 66 (1951).

[12] S. Birnbaum, *Rev. Chim.* (Bucharest), **2**, 77 (1958).

Table I. Thermodynamical Quantities of Gaseous Compounds Related with the Hydrogenation and Hydrogenolysis of Phenol (kcal/mole)

Compound	$-\Delta H^\circ_{f,298}$	$-\Delta F^\circ_{f,298}$	
Phenol	21.71[a]	6.26[a]	(5.12)[d]
Cyclohexanone	59.36[b]		(17.88)[d]
Cyclohexanol	74.78[c]		(25.14)[d]
Benzene	−19.82[a]	−30.99[a]	(−29.35)[d]
Cyclohexene	1.72[a]	−18.20[a]	(−16.71)[d]
Cyclohexane	29.43[a]	− 8.03[a]	(− 6.55)[d]
H_2O	57.80[a]	54.64[a]	(54.61)[d]
1-Cyclohexenol			(7.15)[d]

a) G. Lange, "Handbook of Chemistry," 1964
b) Calculated from the heat of formation of cyclohexanol and the heat of hydrogenation of cyclohexanone.
c) Calculated from the data in liquid phase and the heat of evaporation.
d) Estimated according to Krevelen and Cherimin's method ("Estimation of Thermodynamical Properties of Organic Compounds," Academic Press Inc., New York, 1958).

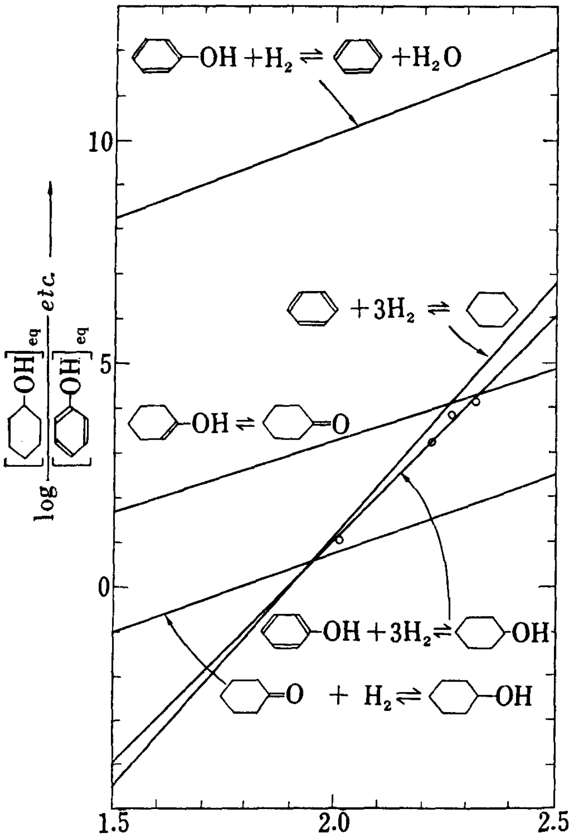


Fig. 1. Equilibrium Data of Some Related Reactions

shall investigate the result of the hydrogenation of phenol in the light of the equilibrium data shown in Fig. 1.

Selectivity of Metals for the Hydrogenation of Phenol

When a sample of phenol was injected into a stream of hydrogen to pass through a given metal catalyst layer kept in the temperature range from 170 to 300°, a chromatogram was obtained with elution peaks corresponding to cyclohexanol, cyclohexanone, benzene and cyclohexane suggesting that both hydrogenation and hydrogenolysis of phenol take place. A typical chromatogram for the reaction products obtained, for example, on iridium at 190° is shown in Fig. 2. Hydrocarbons other than benzene and cyclohexane were also formed as shown by the chromatogram. However, they were not identified.

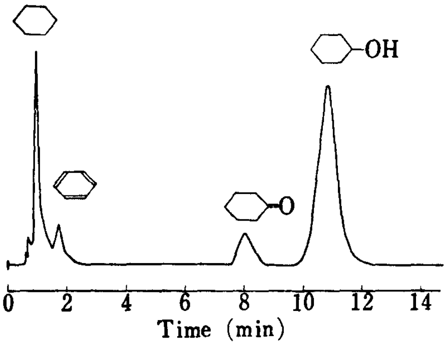


Fig. 2. Chromatogram for the Reaction Products of Phenol with Hydrogen on Iridium at 190°

flow rate of hydrogen: 100 ml/min
sample size: 3.0 μl

The distribution of the products appeared to depend largely on the species of catalyst and reaction temperatures. Let us denote the ratio of cyclohexanol to cyclohexanone formed as

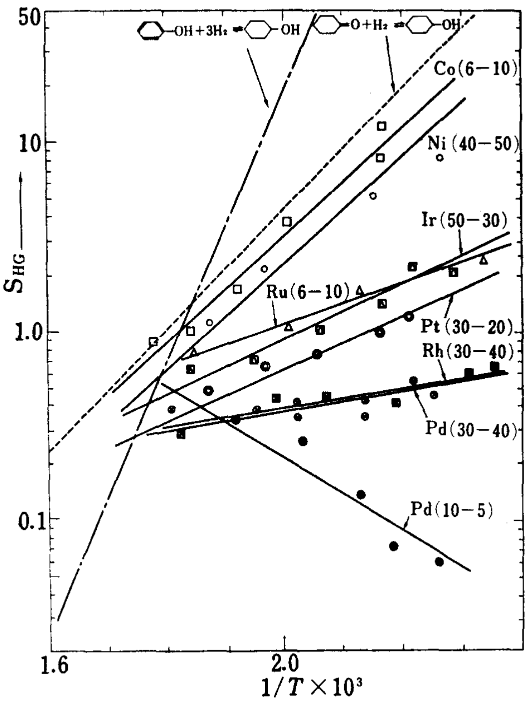
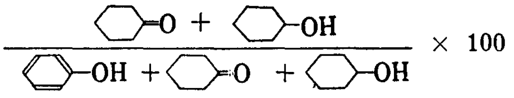


Fig. 3. Temperature Dependency of the Ratio of Cyclohexanol to Cyclohexanone formed during the Hydrogenation of Phenol over Group VIII Metals

S_{HG}. The S_{HG} was then determined on each metal catalyst at various temperatures, assuming that the area under a peak represents the number of molecules present. The dependency of S_{HG} on catalyst species and reaction temperature is shown in Fig. 3, where the number in the bracket shows the degree of conversion defined by



It was found that the S_{HG} is dependent also on the degree of conversion as illustrated in Fig. 3 for palladium.

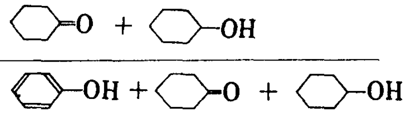
It can be seen from Fig. 3 that the hydrogenation–dehydrogenation between cyclohexanone and cyclohexanol or reaction (2) is nearly equilibrated at high temperatures (around 300°) on most catalysts whereas at low temperatures the S_{HG} varied by a factor of about 100 depending on the kind of catalyst. Cyclohexanol was formed ten times greater than cyclohexanone on cobalt or nickel whereas only one–tenth in the case of low conversion on palladium or one–fifth in the case of high conversion. A similar trend was found also on rhodium. It was noted that cobalt or nickel is so active for the reaction (2) that the S_{HG} was close to equilibrium over the entire temperature range investigated. On the other hand, predominant product was cyclohexanone on palladium or on rhodium, and the S_{HG} on palladium appeared even to decrease with decreasing reaction temperature contrary to its thermodynamical relation especially when the conversion was low.

It goes from Fig. 3 that the relative amount of cyclohexanol over that of cyclohexanone formed or S_{HG} determined on a series of transition metal catalysts is represented by the following sequence around 200°.

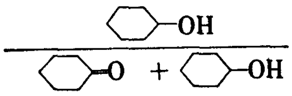
$$\mathrm{Co} \gtrsim \mathrm{Ni} > \mathrm{Ru} > \mathrm{Ir} > \mathrm{Pt} > \mathrm{Rh} \gtrsim \mathrm{Pd} \qquad \text{(a)}$$

In view of the considerable difference in the relative amount of the two major products affected by catalyst species, reaction temperature and also by the extent of reaction, it is tentatively assumed that phenol is hydrogenated to give cyclohexanone first and then to produce cyclohexanol and that the two consecutive steps proceed with different rates depending on both catalyst species and reaction temperature.

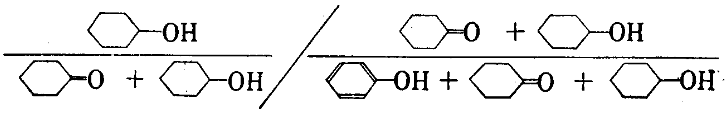
Let us compare the degree of conversion of phenol:



with the degree of hydrogenation of pulsed cyclohexanone:



The latter can be readily obtained when cyclohexanone is injected instead of phenol. The ratio of these two quantities should be regarded as an approximate measure of the relative



easiness of the hydrogenation of cyclohexanone over that of phenol. The ratio may perhaps be insensitive to the degree of conversion because the degree of conversion of cyclohexanone and phenol is cancelled out between the numerator and denominater.

The ratios determined on the metal catalysts of group VIII respectively around 200°C were compared and found to be of the following sequence:

$$\mathrm{Fe}(\infty)>\mathrm{Co}(3.3)>\mathrm{Ru}(2.5)>\mathrm{Ni}(2.0)>\mathrm{Ir}(1.7)>\mathrm{Pt}(1.4)>\mathrm{Rh}(0.7)>\mathrm{Pd}(0.5) \qquad \text{(b)}$$

Apparently, the sequence (b) was nearly parallel with that of (a). We shall discuss this point later.

Selectivity of Metals for the Hydrogenolysis of Phenol

As already mentioned, the catalytic hydrogenation of phenol gave rise to benzene, cyclohexane and some unknown hydrocarbons (see Fig. 2); the breaking of the carbon–oxygen bond of phenol took place to a certain extent depending on reaction temperature and catalyst species. For example ruthenium was

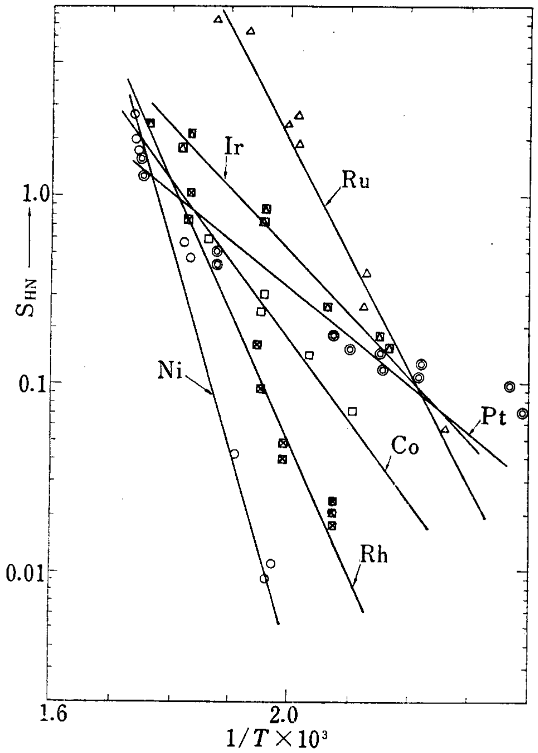


Fig. 4. Temperature Dependency of the Ratio of Hydrogenolysis Products to Hydrogenation Products during the Hydrogenation of Phenol over the Group VIII Metals

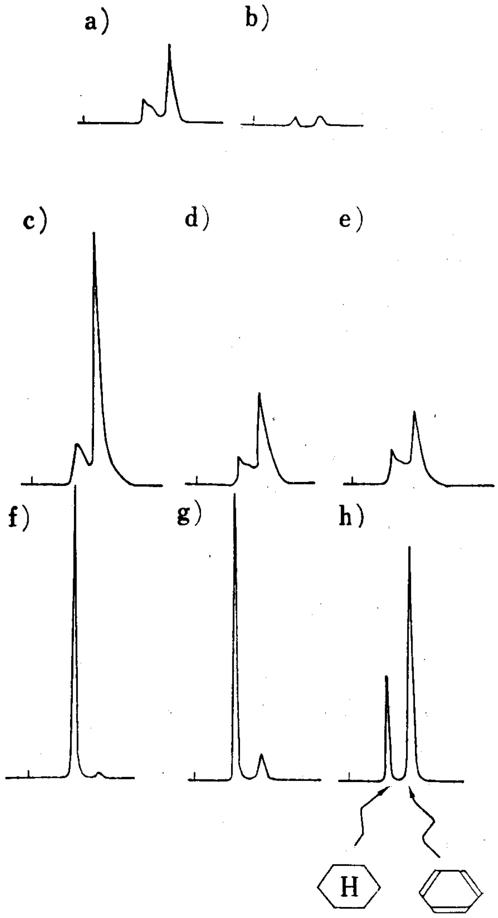


Fig. 5. Hydrogenolysis Products of Phenol over Platinum

a)	190° Pt catalyst	3 μl PhOH injection
b)	190° Pt catalyst	3 μl cyclohexanol injection
c)	240° Pt catalyst	3 μl PhOH injection
d)	240° Pt catalyst	3 μl cyclohexanone injection
e)	240° Pt catalyst	3 μl cyclohexanol injection
f)	240° Pt catalyst	3 μl cyclohexane injection
g)	240° Pt catalyst	3 μl cyclohexene injection
h)	240° Pt catalyst	3 μl benzene injection

most active for the breaking while no hydrogenolysis took place on palladium. Hydrogenolysis took place to a greater extent on platinum than on rhodium in agreement with the result of Smith.[5] The ratio of the amount of fission products to those of hydrogenated species was determined on each catalyst at various temperatures. The result is shown in Fig. 4. The ratio, denoted as S_{HN}, obtained around 200° was of the following sequence:

$$Ru > Ir > Pt > Co > Rh > Ni > Pd \qquad (c)$$

The data for palladium is not shown in Fig. 4 because of no hydrogenolysis activity. Iron was also inactive to the reaction.

Apparently, the sequence for S_{HN} was not in parallel with that for S_{HG}. In other words, the ability to hydrogenate carbonyl group by metals does not seem to correlate with that of the cleavage of the carbon–oxygen bond.

Benzene and cyclohexane were the main fission products at low temperatures on all metals. In particular, platinum–catalysed–hydrogenation gave rise to benzene and cyclohexane exclusively over the entire temperature range investigated as shown by the chromatogram in Fig. 5a and c. On the other hand, hydrocarbons other than six membered ring were formed on iridium even at low temperatures as shown in Fig. 2.

Platinum gave more benzene than cyclohexane around 200° (Fig. 5a and c). The formation of benzene was negligibly small when cyclohexane was injected to the catalyst layer (Fig. 5f). Also benzene was found to be hydrogenated only partly when it was injected (Fig. 5h). Thus, benzene seems to be produced initially. This interpretation was supported by the fact that the increase of the flow rate of hydrogen increased the relative amount of benzene over cyclohexane.

It should be noted that benzene was formed more than cyclohexane even when cyclohexanone or cyclohexanol was injected as shown in Fig. 5b, d and e. The phenomena should be quite unusual because under the experimental circumstance cyclohexane is thermodynamically more stable than benzene (see Fig. 1). Similar phenomena were reported in the hydrogenolysis of cyclohexylamine or of aniline[7,13] on platinum film and nickel–silica–alumina respectively. Phenol injection gave more hydrogenolysates especially benzene than cyclohexanone or cyclohexanol injection (Fig. 5c, d and e). The phenomena were common to iridium, cobalt, nickel and rhodium.

Discussion

Let us consider the reaction scheme shown in Fig. 6 concerning to the catalytic hydrogenation and hydrogenolysis of phenol.

The sequence (b) indicates the relative activity of metals for the process 5 over 2. Therfore, the agreement of the sequence (a) with (b) would suggest that the value of S_{HG} also indicates the relative activity of metals for the process 5 over the process 2.

This interpretation is not in agreement with the opinion advocated by Smith and Stump[5] who considered that cyclohexanol is formed *via* the process 4. The process 3 may probably take place faster than 4 because of the remarkable stability of cyclohexanone as compared with cyclohexanol. Also the shift of double bond in cyclohexenol is expected to proceed faster than its hydrogenation similarly as the case of the hydrogenation of 2,3-dimethylcyclohexene.[9] As already mentioned, Smith and Stump did not measure the rate of the formation of cyclohexanol; instead, they measured the rate of hydrogen uptake. Thus, it seems probable to us that the rate data due to Smith and Stump correspond to those of the hydrogenation of phenol to produce cyclohexanone. It is our opinion that phenol is hydrogenated mainly through process 1, 2, 3, 5, 6, and 7 in agreement with the scheme on nickel proposed by Jungers.

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13) C. Kemball and R. L. Moss, *Trans. Faraday Soc.*, **82**, 154 (1960).

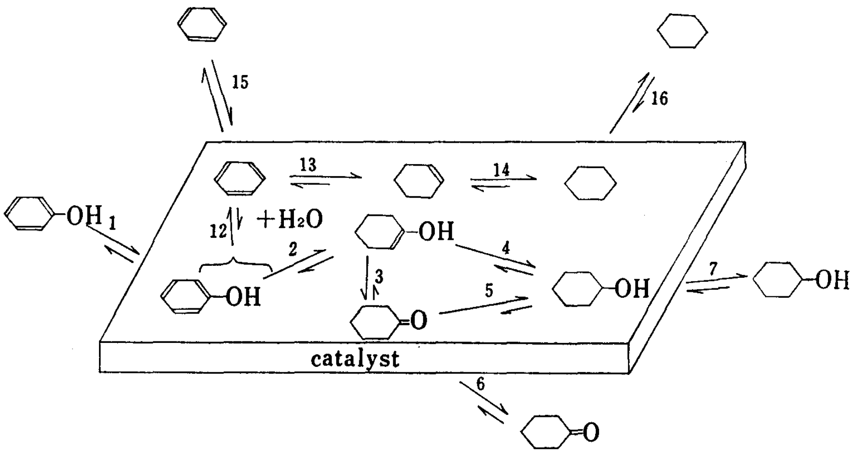

Fig. 6. Reaction Scheme for the Hydrogenation and Hydrogenloysis of Phenol

Cyclohexanone was the main product on either rhodium or palladium when phenol was hydrogenated. Such selectivity for the hydrogenation of phenol was not reported on rhodium while it has been known on palladium.[14] It is generally accepted that palladium has low hydrogenation activity for ketone. For example, the relative activities of metal films for the hydrogenation of acetone or cyclopentanone was reported to be of the sequence:

$$Pt>Ni>Fe>W>Pd>Au$$

according to Kemball and his coworker.[15] The lowest position of palladium in the sequence for S_{HG} is a natural consequence if palladium possesses a low activity for the hydrogenation of cyclohexanone while it catalyzes efficiently the hydrogenation of phenol to produce cyclohexanone. On the other hand, the finding that the hydrogenation–dehydrogenation reaction (2) is almost in equilibrium on cobalt or nickel suggests that these metals are highly active for the hydrogenation of ketone. The position of platinum in the sequence (a) or (b) also suggests that this metal is active for the hydrogenation of both aromatic ring and carbonyl group.

It is generally accepted that hydrogenolysis dominates over hydrogenation with increasing reaction temperature. The activity sequence of metals for propane formation from acetone is reported [15] to be

$$Pt>W>Ni>Pd\approx Au$$

and the hydrogenolysis of cyclopentanone is of the sequence[16]

$$Pt>Pd>Rh>W>Ni$$

The activity sequences of metals for the two hydrogenolysis reactions are not identical. Also our sequence (c) does not seem to agree with these sequences. Further works are required to correlate the activity data for the hydrogenolysis reactions.

The initial formation of benzene from cyclohexanone or from cyclohexanol in the presence of hydrogen should be regarded as unusual. Because, the formation of cyclohexane is thermodynamically feasible under the experimental condition:

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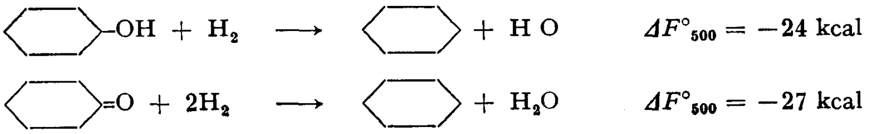
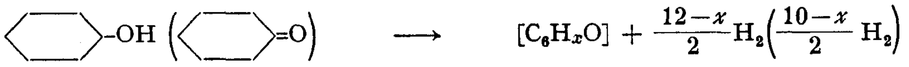
[14] R. J. Duggan, E. J. Murray and L. O. Winstron, U. S. Patent 3076810, Feb. 5, 1963.

[15] C. Kemball and C. T. H. Stoddart, *J. Colloid Sci.*, **11**, 532 (1956).

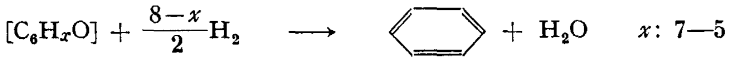
[16] C. Kemball and C. T. H. Stoddart, *Proc. Roy. Soc.* (London), ser. A, **246**, 521 (1958).



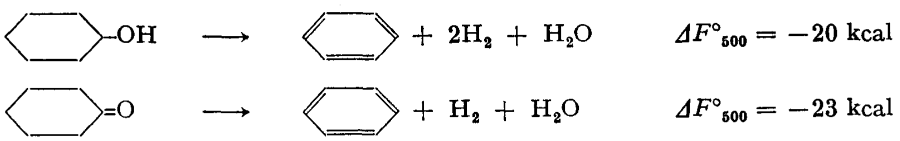
Cyclohexanone or cyclohexanol would probably be adsorbed on metals with dissociation, before the reaction with hydrogen, according to



and adsorbed phenol–like species formed would decompose to produce benzene.



The hydrogenolysis of cyclohexanol or cyclohexanone to yield benzene is not unfavorable thermodynamically:



However, the preferential formation of benzene is of kinetic nature, and would probably be associated with the high activity of metals for stripping hydrogen atoms from cyclohexanone or cyclohexanol.