The Co-amination of Phenol and Cyclohexanol with Palladium-on-carbon Catalyst in the Liquid Phase. An Application of a Hydrogen-transfer Reaction

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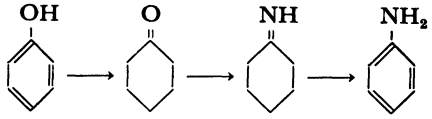
Phenol and Cyclohexanol are simultaneously aminated to aniline and cyclohexylamine by ammonolysis with the palladium-on-carbon catalyst in the liquid phase, although the amination of either phenol or cyclohexanol hardly occurs without the other. In contrast, carbon-supported ruthenium, rhodium, and platinum catalysts are ineffective for this co-amination; they are active only for the amination of cyclohexanol to cyclohexylamine. These results are explained by the specific activity of palladium for hydrogen transfer between phenol and cyclohexanol.

It is well known that the amination of phenol to aniline by ammonolysis catalyzed by acidic catalysts, such as silica-alumina,[1,2] zeolites,[3] and metal chlorides.[4] Supported metal catalysts are known to be effective for the amination of cyclohexanol to cyclohexylamine, the hydroamination of phenol to cyclohexylamine, and the dehydroamination of cyclohexanol to aniline. For example, Richardson and Lu[5] reported that the vapor-phase dehydroamination of cyclohexanol to aniline took place over supported platinum catalysts. Recently, it has been found that these supported metal catalysts, in cooperation with hydrogen or hydrogen-transfer agents, are also effective for the amination of phenol to aniline. Ono and Ishida[6] reported that phenol was successfully aminated to aniline with ammonia and hydrogen over palladium-on-alumina in the vapor phase. We previously reported[7] that phenol was aminated with ammonia with palladium-on-carbon in the presence of cyclohexanone, which is a hydrogen-transfer agent.

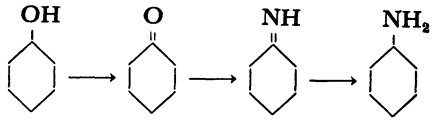
The following reaction pathway has been proposed for the amination of phenol over supported metal catalysts:[7]



(1)

The first step of this scheme is the formation of cyclohexanone due to the hydrogenation of phenol, which means that hydrogen or hydrogen-transfer agents are needed.

On the other hand, the amination of cyclohexanol to cyclohexylamine with ammonia over supported metal catalysts has been considered to proceed through the pathway indicated below.[8] In this case, the first step is the dehydrogenation of cyclohexanol to cyclohexanone.



(2)

Taking these two reaction schemes into consideration, we investigated the possibility of the liquid-phase co-ammonolysis of phenol and cyclohexanol; we have found that phenol and cyclohexanol can be simultaneously aminated with the palladium-on-carbon catalyst.

We have already reported a part of our results in a letter.[9] This paper is a detailed report of this co-amination reaction. The specific catalytic activity of palladium and the reaction scheme are also discussed.

Experimental

Catalysts and Reagents. The 5 wt% metal-on-carbon catalysts were of commercial origin (Nippon Engelhard Co.). The reagents were of a guaranteed reagent grade and were used without further purification except in the case of *N*-cyclohexylaniline, which was prepared by the reaction of phenol and cyclohexylamine using palladium-on-carbon. The ammonia and hydrogen were supplied from gas cylinders.

Procedures. Each experiment was run in a 100-cm^3 stainless-steel autoclave. Unless otherwise specified, phenol, cyclohexanol, and the catalyst were put into the autoclave. The autoclave was sealed, purged with hydrogen, and evacuated successively, and then ammonia was introduced into the autoclave from a pressure-resistant gas-collecting tube. The autoclave thus prepared was set in an electric furnace and heated for the reaction. At the end of each reaction, the autoclave was cooled and the excess ammonia was released. The contents were filtered to remove the catalyst. 2-Propanol was used as a solvent to assist in removing the reaction mixture from the autoclave and in washing the filter cake. The filtered reaction mixture was analyzed by means of gas chromatography. A 5-m column of Silicon DC-550 (20 wt%) on Chromosorb W AW-DMCS, operating at 145 °C, was used to analyze phenol, aniline,

cyclohexylamine, and cyclohexanone. A 3-m column of PEG-20 M (20 wt%) on Chromosorb W AW-DMCS, operating from 130 °C to 220 °C, was used to analyze cyclohexanol, dicyclohexylamine, *N*-cyclohecylaniline, and diphenylamine.

Results and Discussion

Need of Coexistence of Phenol and Cyclohexanol for Co-amination. Mixtures of phenol and cyclohexanol in various compositions were allowed to react with ammonia in the presence of palladium-on-carbon at 250 °C for 3 h. Figure 1 shows the effect of the mixture composition. Aniline and cyclohexylamine were obtained in high yields when nearly equal amounts of phenol and cyclohexanol were used, but the amination of phenol or cyclohexanol alone hardly took place at all. The maximum aniline yield was obtained at a 50% phenol content, while the cyclohexylamine yield reached its maximum value at a 20% phenol content. From these results, it is concluded that the amination of phenol and cyclohexanol with the palladium-on-carbon catalyst is promoted by the coexistence of the two components. *N*-cyclohexylaniline and dicyclohexylamine were also obtained as by-products. These by-products are considered to be formed by means of condensation reactions.

Effect of Reaction Temperature. The effect of the reaction temperature of the co-ammonolysis of equal amounts of phenol and cyclohexanol was examined in the temperature range of 200—270 °C with the palladium-on-carbon catalyst. As is shown in Fig. 2, the product yields increased with the reaction temperature. It should be noted thet the aniline yield was always higher than the cyclohexylamine yield, and that a considerable amount of *N*-cyclohexylaniline was formed at higher temperatures.

Effect of Ammonia Amount. Figure 3 shows the effect of the amount of ammonia. As can be seen in this figure, the product distribution changed greatly with the amount of ammonia. When phenol and cyclohexanol were allowed to react in the absence of ammonia, cyclohexanone was formed as the only product because of the hydrogen-transfer from cyclohexanol to phenol.

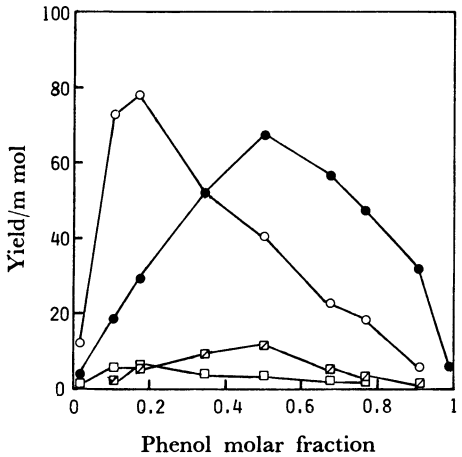


Fig. 1. Ammonolysis of phenol and cyclohexanol with various composition. Phenol and cyclohexanol (total 0.2 mol) are allowed to react with ammonia (1 mol) at 250 °C for 3 h over Pd/C (1 g).
●: Aniline yield, ○: cyclohexylamine yield, ⊠: *N*-cyclohexylaniline yield ×2, □: dicyclohexylamine yield ×2.

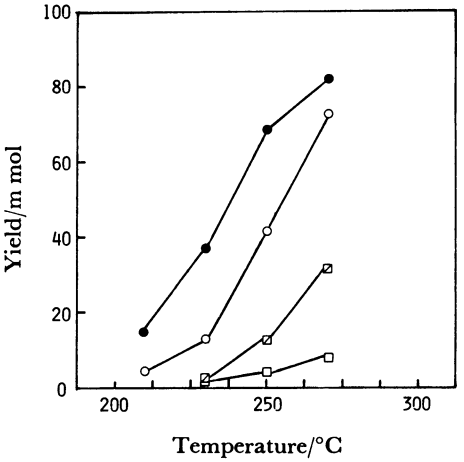


Fig. 2. Effect of reaction temperature on the co-amination. Phenol (0.1 mol) and cyclohexanol (0.1 mol) are allowed to react with ammonia (1 mol) for 3 h over Pd/C (1 g).
●: Aniline yield, ○: cyclohexylamine yield, ⊠: *N*-cyclohexylaniline yield ×2, □: dicyclohexylamine yield ×2.

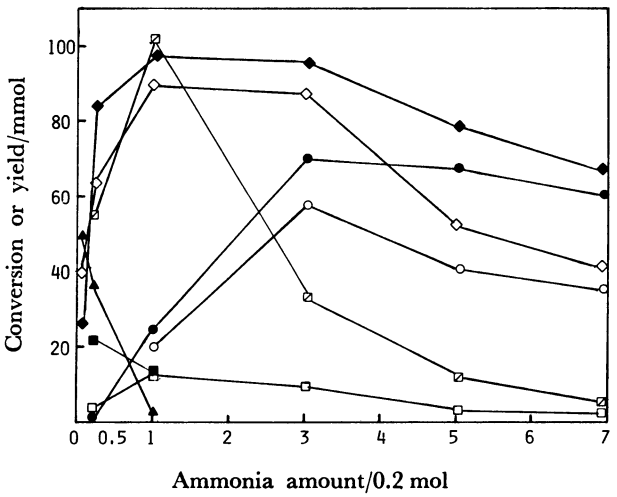


Fig. 3. Effect of ammonia amount on the co-amination. Phenol (0.1 mol) and cyclohexanol (0.1 mol) are allowed to react with ammonia at 250 °C for 3 h over Pd/C (1 g).
◆: Phenol conversion, ◇: cyclohexanol conversion, ●: aniline yield, ○: cyclohexylamine yield, ▲: cyclohexanone yield, ■: diphenylamine yield ×2, ⊠: *N*-cyclohexylaniline yield ×2, □: dicyclohexylamine yield ×2.

When the amount of ammonia increased to 0.2 mol, which was equivalent to the molar quantities of phenol plus cyclohexanol, the cyclohexanone yield decreased rapidly, while amination products composed mainly of *N*-cyclohexylaniline were observed to increase in yield. In this case, there was also a little formation of dicyclohexylamine, diphenylamine, aniline, and cyclohexylamine.

When the amount of ammonia increased in the ranges beyond 0.2 mol, the conversions of phenol and cyclohexanol gradually decreased again; the yields of *N*-cyclohexylaniline and dicyclohexylamine also decreased. Therefore, the selectivities to aniline and cyclohexylamine increased. In the presence of excess ammonia, the main products shifted to aniline and cyclohexylamine.

Effect of Reaction Time. The effect of the reaction time is shown in Fig. 4. The conversions and yields increased with the reaction time. It is noteworthy that the formation of aniline from phenol prevailed over that of cyclohexylamine from cyclohexanol at the initial stage of reaction.

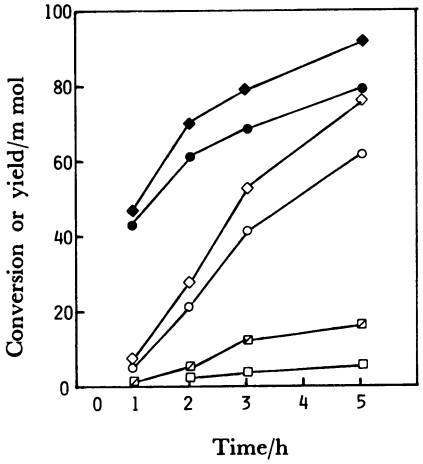
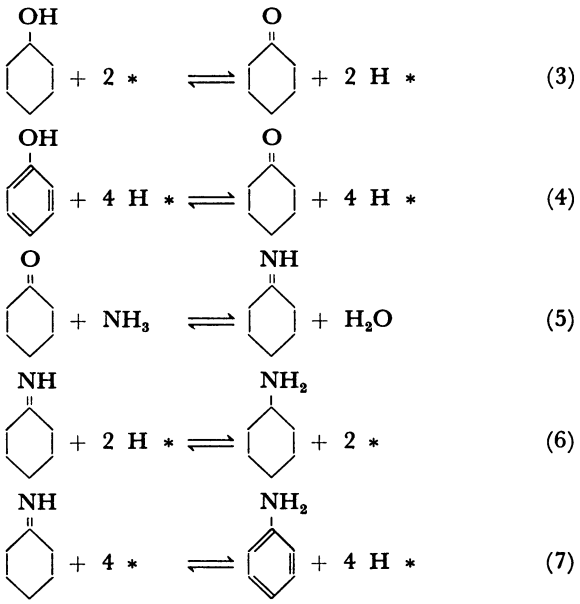


Fig. 4. Effect of reaction time on the co-amination. Phenol (0.1 mol) and cyclohexanol (0.1 mol) are allowed to react with ammonia (1 mol) at 250 °C over Pd/C (1 g).
◆: Phenol conversion, ◇: cyclohexanol conversion, ●: aniline yield, ○: cyclohexylamine yield, ⊠: *N*-cyclohexylaniline yield ×2, □: dicyclohexylamine yield ×2.

Cataltic Activities of Carbon-supported Platinum-group Metals. The catalytic activities of various carbon-supported platinum-group metals are compared in Table 1. As may be seen in this table, palladium was the only effective catalyst for the co-amination. Ruthenium, rhodium, and platinum were ineffective for the co-amination, and aniline was not formed from phenol, though the amination of cyclohexanol to cyclohexylamine did occur.

Reaction Scheme of Co-amination. The co-amination of phenol and cyclohexanol with the palladium-on-carbon catalyst is considered to proceed through the following reaction steps:



In these equations, * and H* represent an empty catalytic site and an adsorbed hydrogen atom respectively.

In the absence of cyclohexanol, the amination of phenol cannot occur because there is no adsorbed hydrogen, which is necessary for Eq. 4. However, in the co-existence of phenol and cyclohexanol, they are effectively converted into cyclohexanone through hydrogen-transfer by Eqs. 3 and 4. In fact, the formation of a large amount of cyclohexanone by the reaction of phenol and cyclohexanol was observed in the absence of ammonia (Fig. 3). The resulting cyclohexanone reacts easily with ammonia to be converted into cyclohexanimin (Eq. 5), which is either hydrogenated

Table 1. Activities of carbon-supported platinum-group metal catalysts

Catalyst	Product (Yield/m mol)			
	Aniline	Cyclohexylamine	*N*-Cyclohexylaniline	Dicyclohexylamine
Pd/C	68	41	6.0	1.9
Ru/C	0	71	0	0
Rh/C	4.0	44	0	0
Pt/C	1.9	74	0	0

Phenol (0.1 mol) and cyclohexanol (0.1 mol) are allowed to react with ammonia (1 mol) in the presence of a catalyst (1 g) at 250 °C for 3 h.

TABLE 2. AMMONOLYSIS OF PHENOL-CYCLOHEXYLAMINE OR ANILINE-CYCLOHEXANOL MIXTURES

Reactant	Product (Yield/m mol)					
	Phenol	Cyclohexanol	Aniline	Cyclohexylamine	*N*-Cyclohexylaniline	Dicyclohexylamine
Phenol-cyclohexylamine	9.3	0.7	68	77	18	3.8
Aniline-cyclohexanol	0	63	98	32	3.2	1.4

The reactant mixtures (0.1 mol+0.1 mol) are allowed to react with ammonia (1 mol) in the presence of Pd/C (1 g) at 250 °C for 3 h.

to cyclohexylamine (Eq. 6) or dehydrogenated to aniline (Eq. 7).

Figures 2 and 4 suggest that the amination of phenol to aniline (Steps 4, 5, and 7) prevails over that of cyclohexanol to cyclohexylamine (Steps 3, 5, and 6) in the early stages of the reaction. The factor which determines the ratio of these two reaction rates is not clear, but the concentration of adsorbed hydrogen may play an important role.

Taking the above reaction schemes into consideration,it is conceivable that the amination rate of phenol to aniline is accelerated in the presence of cyclohexylamine, because hydrogen-transfer can take place between phenol and cyclohexylamine. Also, the amination rate of cyclohexanol to cyclohexylamine may be accelerated in the presence of aniline. In order to examine the probable validity of these assumptions, phenol–cyclohexylamine and cyclohexanol–aniline mixtures were allowed to react with ammonia in the presence of the palladium-on-carbon catalyst. The results, shown in Table 2, support these assumptions.

Specificity of Palladium. As has been mentioned above, palladium-on-carbon was the only effective catalyst for the co-amination of phenol and cyclohexanol among the carbon-supported platinum-group metal catalysts. This specificity could be interpreted in terms of its specific catalytic activity for hydrogen-transfer reactions.

To get further insights into the specificity of palladium, the hydroamination of phenol was studied. Figure 5 shows the effect of the initial hydrogen pressure on the hydroamination of phenol with carbon-supported palladium. The yields of cyclohexylamine and dicyclohexylamine as well as the phenol conversion increased with an increase in the hydrogen pressure. It should be noted that considerable amounts of aniline were formed, along with *N*-cyclohexylaniline, at low hydrogen pressures. Figure 6 shows the effect of the reaction time. It is also worth noting that cyclohexylamine and dicyclohexylamine were formed at an early stage of the reaction, and that aniline and *N*-cyclohexylaniline increased in their yields with the reaction time. The latter result is consistent with the results in Table 2.

In order to compare the ruthenium catalyst with palladium, the hydroamination of phenol with

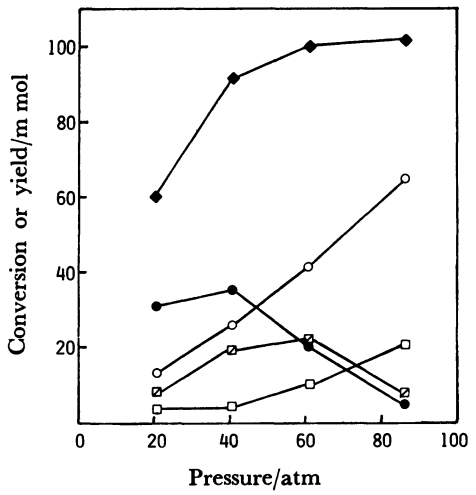


Fig. 5. Effect of initial hydrogen pressure on the hydroamination of phenol over Pd/C. Phenol (0.1 mol) is allowed to react with ammonia (0.6 mol) and hydrogen at 250 °C for 3 h over Pd/C (0.5 g).
◆: Phenol conversion, ●: aniline yield, ○: cyclohexylamine yield, ⊠: *N*-cyclohexylaniline yield ×2, □: dicyclohexylamine yield ×2.

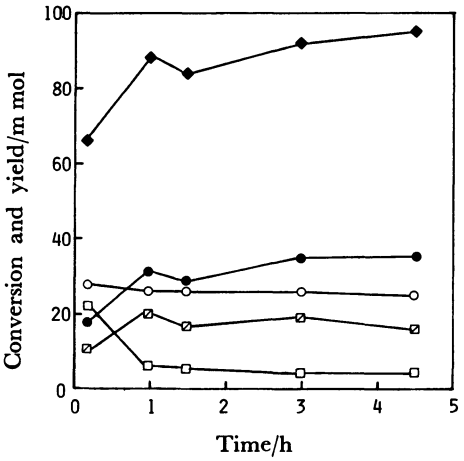


Fig. 6. Effect of reaction time on the hydroamination of phenol over Pd/C. Phenol (0.1 mol) is allowed to react with ammonia (0.6 mol) and hydrogen (40 atm) at 250 °C over Pd/C (0.5 g).
◆: Phenol conversion, ●: aniline yield, ○: cyclohexylamine yield, ⊠: *N*-cyclohexylaniline yield ×2, □: dicyclohexylamine yield ×2.

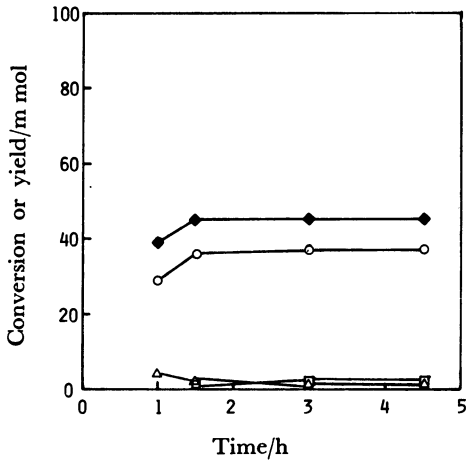


Fig. 7. Effect of reaction time on the hydroamination of phenol over Ru/C. Phenol (0.1 mol) is allowed to react with ammonia (0.6 mol) and hydrogen (40 atm) at 250 °C over Ru/C (0.5 g).
◆: Phenol conversion, ○: cyclohexylamine yield, △: cyclohexanol yield, □: dicyclohexylamine yield ×2.

ruthenium-on-carbon was studied. The effect of the reaction time is shown in Fig. 7. In this case, aniline was not formed, although the hydroamination of phenol to cyclohexylamine did take place. Therefore, it is concluded that ruthenium cannot catalyze hydrogen-transfer reactions. This conclusion might also apply to the cases of rhodium and platinum.

From these results, it is clear that the specificity of palladium is due to its unique catalytic activity for hydrogen-transfer reactions. Further work is necessary to elucidate the reason for this specificity of palladium.

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