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LIQUID PHASE CO-AMMONOLYSIS OF PHENOL AND CYCLOHEXANOL WITH PALLADIUM-ON-CARBON CATALYST

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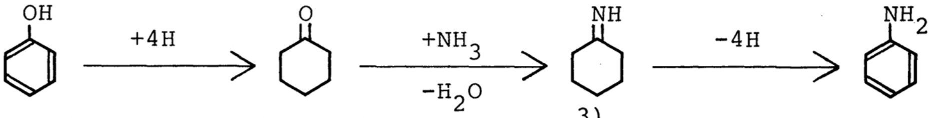
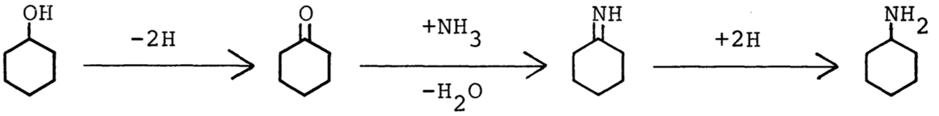
In the presence of Pd/C catalyst, phenol and cyclohexanol are aminated simultaneously to aniline and cyclohexylamine by ammonolysis, while conversion of phenol or cyclohexanol alone is very poor. It is suggested that this amiantion is caused by hydrogen transfer between phenol and cyclohexanol. Ru/C, Rh/C, and Pt/C are ineffective for this co-amination.

It is well known(1) that the ammonolysis of phenol to aniline is catalyzed by a solid acid catalyst such as silica-alumina. In the previous paper,(2) we have reported that phenol is also successfully aminated to aniline with Pd/C in the presence of cyclohexanone and that the amination pathway is shown by Scheme 1. In the first step of this scheme, cyclohexylamine, formed by the ammonolysis of cyclohexanone, is suggested to act as a hydrogen donner.



(Scheme 1)

On the other hand, Guyot and Fournier(3) stated that the amination pathway of cyclohexanol to cyclohexylamine is shown by Scheme 2. In this scheme the first step is dehydrogenation of cylochexanol.



(Scheme 2)

Taking these two schemes into consideration, hydrogen transfer is likely to occur from cyclohexanol to phenol over Pd/C. If so, it may be possible to aminate phenol and cyclohexanol simultaneously by co-ammonolysis. Therefore, we have examined the liquid phase co-ammonolysis of phenol and cyclohexanol with Pd/C catalyst.

Ammonolysis was conducted in a 100 ml stainless steel autoclave. The products were analyzed by gas chromatography.

As is seen from Table 1, phenol and cyclohexanol are simultaneously aminated to aniline and cyclohexylamine in high yields, though conversion of phenol or cyclohexanol alone is very poor. These results suggest that hydrogen transfer should take place between phenol and cyclohexanol. But further work will be necessary to elucidate the reaction mechanism.

Catalytic activities of Ru/C,Rh/C, and Pt/C were also examined in the co-ammonolysis of phenol and cyclohexanol. The results are shown in Table 2. These three catalysts were ineffective for the amination of phenol. This is probably because it is difficult for hydrogen trasfer to occur over Ru/C, Rh/C,and Pt/C. But it was found that the amination of cyclohexanol to cyclohexylamine took place smoothly.

Table 1 Co-ammonolysis of Phenol and Cyclohexanol with Pd/C

Reactant Amount(mmol)		Conversion(mmol)		Product Amount(mmol)	
Phenol	Cyclohexanol	Phenol	Cyclohexanol	Aniline	Cyclohexylamine
201	0	6	———	6	0
181	20	36	8	32	6
151	49	52	22	48	19
134	66	66	29	58	23
100	100	79	53	68	41
67	132	62	68	53	53
34	166	32	87	30	79
20	179	20	79	19	74
0	199	———	14	3	13

Phenol and cyclohexanol were heated with NH_3(1 mol) in the presence of 5% Pd/C(1 g) at 250°C for 3 hr.

Table 2 Activities of the Group VIII Metal-on-carbon Catalysts

Catalyst	Reactant Amount(mmol)		Conversion(mmol)		Product Amount(mmol)	
	Phenol	Cyclohexanol	Phenol	Cyclohexanol	Aniline	Cyclohexylamine
Pd/C	100	100	79	53	68	41
Ru/C	100	100	5	73	0	71
Rh/C	100	100	10	48	4	44
Pt/C	101	100	7	81	2	74

Phenol and cyclohexanol were heated with NH_3(1 mol) in the presence of a 5% metal-on-carbon catalyst(1 g) at 250°C for 3 hr.

References

1) M. Becker and J. Russel, Chem. Eng., 80, April 2, 42 (1973).
2) H. Hamada, T. Matsuzaki, and K. Wakabayashi, Nippon Kagaku Kaishi, 1979, 248.
3) A. Guyot and M. Fournier, Bull. Soc. Chim., 47, 203 (1930).

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