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HOMOGENEOUS CATALYTIC REDUCTION OF AROMATIC NITRO-COMPOUNDS BY HYDROGEN TRANSFER

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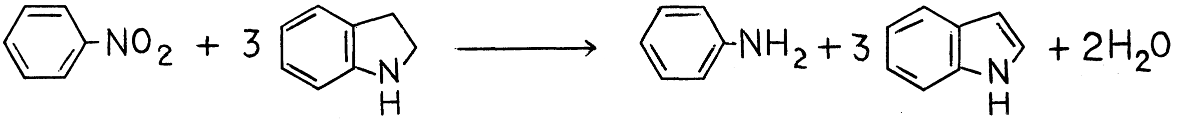
In the presence of noble metal salts, indoline reduced aromatic nitro-compounds to the corresponding aromatic amines under mild reaction conditions.

There have been several reports on the catalytic reduction of nitrobenzenes with molecular hydrogen.[1] However, the reduction with organic hydrogen donors has been scarcely reported. It has been reported that cyclohexene reduced nitrobenzenes in the presence of Pd-carbon,[2] and methanol did in the presence of dodecacarbonyltriiron.[3] We now report that several noble metal salts catalyzed the hydrogen transfer from cyclic amines to nitrobenzenes to give the corresponding anilines.

When nitrobenzene (0.5 M), indoline (1.5 M), and $RhCl_3 \cdot 3H_2O$ (0.08 M) were heated in toluene at 80° C for 4 hr, aniline was obtained in 82 % yield (0.41 M) along with the dehydrogenation product, indole (1.30 M). Other products, such as azo- and azoxy-compounds, were not detected. The identification and the evaluation of the yield of the products were carried out by glc analysis. These results show the following reaction proceeded stoichiometrically.



When indoline was used as a hydrogen donor in the reduction of nitrobenzene, the catalytic activity of noble metal salts decreased in the order; $RuCl_3.nH_2O$ (88 %), $RhCl_3 \cdot 3H_2O$ (82 %), $PdBr_2$ (50 %), $PdCl_2$ (20 %), $ReCl_5$ (5 %), $(NH_4)_2PdCl_4$ (3 %), K_2PtCl_4 (2 %). Here, the percentages shown in the parentheses are the yield of aniline. Fe(II), Co(II), and Ni(II) salts and the phosphine complexes, such as $RhCl(PPh_3)_3$, $RuCl_2(PPh_3)_3$, $RhH(PPh_3)_4$, and $RuH_2(PPh_3)_4$ hardly catalyzed the reduction. Pd-black and Pd-carbon (20 g/liter) gave the yield of 52 % and 15 %, respectively.

When $RhCl_3 \cdot 3H_2O$ (0.08 M) was used as a catalyst in the reduction of nitrobenzene, the hydrogen donating ability of cyclic amines decreased in the order; indoline (82 %), tetrahydroquinoline (15 %), piperidine (3 %), pyrroridine (2 %). Here, the percentages shown in the parentheses are yield of aniline. Cyclohexylamine, morpholine, tri-n-propylamine, and N-methylpiperidine did not reduce nitrobenzene. 2-Propanol, 1-propanol, dioxane, tetrahydrofuran, tetralin, and indan had no hydrogen-donating ability. As nitrobenzenes seem to have strong coordinating power by the high degree of N-O bond polarization,[4] the hydrogen donors with strong coordinating power may be effective for the reduction of nitrobenzenes. This is the reason why amines were the effective hydrogen donors.

Table. The initial rate of the reduction of nitrobenzenes[a)]

$X\text{-}C_6H_4NO_2$ X	rate, mol l^{-1} min^{-1} x 10^4	$X\text{-}C_6H_4NO_2$ X	rate, mol l^{-1} min^{-1} x 10^4
p-Cl	33.9	p-OCH_3	5.0
p-$COCH_3$	32.0	p-CH_3	4.3
H	23.4	p-NH_2	4.2
o-Cl	11.0	m-CH_3	4.0
m-Cl	6.7	o-CH_3	3.1
m-OH	6.3	o-OH	1.7
p-OH	5.2		

a) $RhCl_3 \cdot 3H_2O$ (0.08 M), $X\text{-}C_6H_4NO_2$ (0.5 M), and indoline (1.5 M) were heated in dioxane at 80° C.

Substituted nitrobenzenes also were reduced to the corresponding amines under mild conditions. The rates of the reduction of nitrobenzenes are summarized in Table. As for para substituted nitrobenzenes, the reduction rates decreased in the order; p-Cl > p-$COCH_3$ > H > p-OH > p-OCH_3 > p-CH_3 > p-NH_2. Nitrobenzenes with electron-withdrawing groups seem to be reduced faster than those with electron-donating groups.

β-Phenylhydroxylamine, nitrosobenzene, hydrazobenzene, and azobenzene were also reduced to aniline in similar systems, with this order of the ease of the reduction.

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