CHEMISTRY LETTERS, pp. 855-856, 1976. Published by the Chemical Society of Japan

CLEAVAGE OF CARBON-HALOGEN BOND BY THE HYDROGEN TRANSFER FROM ORGANIC COMPOUNDS CATALYZED BY NOBLE METAL SALTS

Hideaki IMAI, Takeshi NISHIGUCHI, Motoo TANAKA,
and Kazuo FUKUZUMI
Department of Applied Chemistry, Faculty of Engineering,
Nagoya University, Chikusa-ku, Nagoya 464

In the presence of noble metal salts, especially Pd(II) salts, the carbon-halogen bond of aryl halides underwent hydrogenolysis with organic hydrogen donors such as indoline and tetrahydroquinoline, and the corresponding aryl compounds and hydrogen halides were formed. The addition of bases promoted the hydrogenolysis.

There are few studies about the catalytic hydrogenolysis of carbon-halogen bond by the hydrogen transfer from organic compounds.1) As for the homogeneous transfer hydrogenolysis, the reduction of polychloroalkyl compounds with alcohols catalyzed by $RuCl_2(PPh_3)_3$ has been reported.2) We report here that several noble metal salts catalyze the hydrogenolysis of aryl halides with organic hydrogen donors.

When a methanol solution (0.5 ml) of $PdCl_2$(0.056 M), indoline (0.50 M), and chlorobenzene (0.50 M) was heated at 140° C for 4 hr in an ampoule sealed under vacuum, benzene (76 %) was obtained together with the dehydrogenation product, indole (88 %). Biphenyl was not detected. The identification and the estimation of the yield of the products were carried out by glc analysis. Several alcohols were examined as a solvent, and the yield of benzene, which is shown in the parentheses, decreased in the order; methanol (76 %), cyclohexanol (68 %), ethanol (40 %), 1-propanol (37 %), 1-butanol (12 %), benzyl alcohol (1 %). Hereafter, methanol was used as a solvent.

When indoline was used as a hydrogen donor in the hydrogenolysis of chlorobenzene under the condition described above, the catalytic activity of noble metal salts decreased in the order; $PdCl_2$ (76 %), $(NH_4)_2PdCl_4$ (75 %), $RhCl_3\cdot3H_2O$ (59 %), $PdBr_2$ (50 %), $IrCl_3$ (32 %), K_2PtCl_4 (12 %), $RuCl_3$ nH_2O (3 %), K_2PtCl_6 (3 %). $ReCl_5$, Fe(II), Co(II), and Ni(II) salts hardly catalyzed the hydrogenolysis. Pd(II) salts were found to have excellent catalytic activities. In the presence of $PdCl_2$, the hydrogen-donating ability of several organic compounds decreased in the order; indoline (76 %), tetrahydroquinoline (42 %), pyrrolidine (28 %), N-methylpyrrolidine (25 %), 3-pyrroline (24 %), piperidine (16 %), 2,5-dihydofuran (7 %), N-methylpiperidine (4 %). Alcohols, which were used as solvents, tetralin, and formic acid showed no hydrogen-donating ability. This result shows that the cyclic secondary amines are the effective hydrogen-donors.

As to halobenzenes, PhX, the yield of benzene decreased in the order; X = Cl > I > Br (Table), and PhF did not react. The ease of oxidative addition of PhX to Pd(0) complex was reported to be in the order; X = Cl < Br < I.3) The hydrogen halides formed poisoned the catalyst and the poisoning effect of HX is presumed to increase in the order; HCl < HBr < HI, because the retarding effect caused by the addition of KX and HX increased in the order; KCl < KBr < KI and HCl < HBr < HI, respectively. Therefore, the order of the yield of benzene is inferred to be realized by the balance between the ease of oxidative addition of PhX to Pd(0) species and the poisoning power of HX formed. An aliphatic halide, octyl chloride, was scarcely hydrogenolyzed.

Table. Transfer hydrogenolysis of aryl halides[a)]

Substrate	Additive (M)	Yield of benzene, %
Chlorobenzene	None	27
	KOH (0.50)	64
	CH_3COONa (0.50)	61
	Na_2CO_3 (0.50)	56
	Cyclohexylamine (0.10)	37
	Cyclohexylamine (0.25)	53
	Cyclohexylamine (0.60)	21
	KCl (0.25)	24
	KBr (0.25)	14
	KI (0.25)	trace
	H_2O (0.25)	31
	HCl aq (0.25)	5
	HBr aq (0.25)	2
	HI aq (0.25)	trace
Chlorobenzene[b]	None	76
Bromobenzene[b]	None	39
Iodobenzene[b]	None	53
Benzylchloride[b]	None	45[c]

a) $PdCl_2$ (0.056 M), the substrate (0.50 M), and indoline (0.50 M) were heated in methanol at 80° C for 1 hr. b) This reaction was carried out at 140° C for 4 hr. c) This is the yield of toluene formed.

When bases, such as KOH, CH_3COONa, and cyclohexylamine, were added to the reaction system, the yield of benzene increased. The role of the bases may be the removal of the HX which is the poison of the catalyst. The addition of larger amount (0.60 M) of cyclohexylamine lowered the yield of benzene. This result suggests that too much bases retarded the hydrogenolysis by the coordination on the catalyst. The poisoning effect of PPh_3, indole, acetic acid anhydride, and pyridine was also confirmed.

As the mechanism of transfer hydrogenolysis of aryl halides, we propose the following reaction scheme.

$$
\begin{aligned}
&PdCl_2 + DH_2 \longrightarrow Pd^0 + De + 2\,HCl \qquad && DH_2 = \text{Hydrogen donor}\\
&Pd^0 + ArX \longrightarrow Ar\text{-}Pd\text{-}X && De = \text{Dehydrogenated donor}\\
&Ar\text{-}Pd\text{-}X + DH_2 \longrightarrow ArH + H\text{-}Pd\text{-}X + De &&\\
&H\text{-}Pd\text{-}X \longrightarrow Pd^0 + HX &&
\end{aligned}
$$

References

1) K. Kindler and K. Luhrs, Chem. Ber., 99, 227 (1966); E. A. Braude, R. P. Linstead, K. R. H. Wooldridge, and P. W. D. Mitchell, J. Chem. Soc., 3595 (1954).
2) Y. Sasson and G. L. Rempel, Tetrahedron Lett., 36, 3221 (1974); Y. Sasson and G. L. Rempel, Synthesis, 448 (1975).
3) P. Fitton and E. A. Rich, J. Organometal. Chem., 28, 287 (1971).

(Received June 3, 1976)