CHEMISTRY LETTERS, pp. 1679-1682, 1991.

Selective Catalytic Reduction of Aromatic Nitro Compounds Affording Amines under CO/H_2O Conditions Using Amine-added Ruthenium-Carbonyl Complexes

Kotohiro NOMURA*
Organic Synthesis Research Laboratory, Sumitomo Chemical Co. Ltd.,
10-1, 2-Chome Tsukahara, Takatsuki, Osaka 569

Remarkably high selectivities of nitro-group as well as high catalytic activities for the reduction of aromatic nitro compounds affording corresponding amines under CO/H_2O conditions are exhibited by using amine(HNR_2)-added Ru-carbonyl complexes; the reduction also proceeded without by-producing H_2 which was formed by the Water-Gas Shift Reaction.

Water-Gas Shift Reaction has been one of the most important processes from the aspect of industrial utilization of carbon monoxide and of a pure hydrogen source.[1] As one of its applications, organic synthesis under CO/H_2O conditions,[2] especially the reduction of aromatic nitro compounds using homogeneous catalysts has also drawn considerable attention.[2,3] However, the efficient reduction with high catalytic activity as well as with high selectivity has not so far been reported.[4]

$$ArNO_2 + 3CO + H_2O \longrightarrow ArNH_2 + 3CO_2$$

In this paper, we wish to present amine(HNR_2)-added Ru-carbonyl complexes which show not only high catalytic activities but also remarkably high selectivities of nitro-group for this reaction.[5]

The reductions were typically carried out as follows: in an autocarve (110 or 50 ml) made of stainless steel (SUS 316) and equipped with a stirrer derivable by magnetic force, were charged $Ru_3(CO)_{12}$ (0.003 mmol), prescribed amount of amine, ethanol (10 ml), water (4 ml) and nitrobenzene (ca. 10 mmol). The reaction mixture was stirred under CO (20 atm) at 150 °C for 100 min. The reaction product was then analyzed by GLC using internal standard and was identified using GLC by co-injection with an authentic sample (column OV-225, 3 m) and GC-MS (QP-1000, Shimazu Co. Ltd.). The reaction product was only aniline from nitrobenzene.

The results for the reduction of $PhNO_2$ catalyzed by various amine-added $Ru_3(CO)_{12}$ complexes are summarized in Table 1. The reduction proceeded at significant rates under above mentioned reaction conditions. It should be noted that the rate remarkably increased upon the addition of only a small amount of amines (HNR_2);[6] especially, diisopropylamine and dibutylamine were preferable. The other amines such as pyrrolidine, piperidine were also effective. It was also revealed that effective ratio of amine additives were different. The important fact was also found that the rate markedly increased at higher reaction temperature, much higher catalytic activity may be exhibited at higher reaction temperature and under higher CO pressure.

Table 1. Amine-added $Ru_3(CO)_{12}$ catalyzed reduction of $PhNO_2$ under CO/H_2O conditions

No.	Amine	Molar Ratio	Temp /°C	Turnovers /mol-cat^{-1}
1	pyrrolidine	5	150	1573
2	piperidine	3	150	1524
3	piperidine	3	180	3422$^{a)}$
4	$HN(i\text{-}Pr)_2$	50	150	1683
5	$HN(i\text{-}Pr)_2$	50	180	3421$^{a)}$
6	$HN(i\text{-}Pr)_2$	70	150	2016
7	$HNEt_2$	25	150	1510
8	$HNEt_2$	25	180	3448$^{a)}$
9	$HNBu_2$	35	150	1883
10	$HN(c\text{-}C_6H_{11})_2$	50	150	1694

a) >98% yield.

Table 2. $Ru_3(CO)_{12}$-$HN(i\text{-}Pr)_2$ catalyzed reduction of $PhNO_2$ using CO and water

No.	Solvents	Turnovers /mol-cat^{-1}
6	ethanol	2016
11	methanol	1707
12	3-methyl-1-butanol	1665
13	diglyme	1944
14	acetone	1919

As revealed from Table 2, which shows the results using some solvents, in place of ethanol, under same conditions in Table 1, other solvents can be used on this catalytic reaction.

It should also be paid particular attention that the reduction catalyzed by $HN(i\text{-}Pr)_2$-added $Ru_3(CO)_{12}$ proceeded with remarkably high selectivities of nitro-group as shown in Table 3. Aromatic nitro compounds with halogen substituents were reduced to give corresponding amines; p-cyanonitrobenzene and p-nitrobenzophenone were also reacted to afford p-aminobenzonitrile and p-aminobenzophenone, respectively, without reducing C=O and C≡N bond.[7] It should also be noted that the reduction of acetophenone, phenylacetylene and benzonitrile did not proceed under the same conditions in Table 3. These results, that aromatic nitro-group was reduced almost exclusively, are very important from both the synthetic and the industrial point of view.

Table 3. $Ru_3(CO)_{12}$-HN(i-Pr)$_2$ catalyzed reduction of aromatic nitro compounds using CO and water a)

Substrates	Products	Yield/%
o-chloronitrobenzene	p-chloroaniline	>99.9
o-bromonitrobenzene	o-bromoaniline	>99.9
p-chloronitrobenzene	p-chloroaniline	>99.9
p-cyanonitrobenzene	p-aminobenzonitrile	>99.9
p-nitrobenzophenone	p-aminobenzophenone	>99.9
acetophenone	reaction did not proceed	
phenylacetylene	reaction did not proceed	
benzonitrile	reaction did not proceed	

a) Reaction conditions: $Ru_3(CO)_{12}$ 0.01 mmol, HN(i-Pr)$_2$ 1.5 mmol, diglyme/H_2O = 15/5 ml, $ArNO_2$ 5 mmol, CO 20 atm, 150 °C, 2 h.

Furthermore, considerable attention should be paid that stoichiometric amount of CO_2 (ca. 14.7 mmol) was formed at the end of the reduction of o-chloronitrobenzene affording o-chloroaniline without by-producing H_2 (ca. 0.4 mmol), whereas no production of CO_2 and quite a trace amount of H_2 (ca. 0.4 mmol) were detected in the reduction of benzonitrile under the same reaction conditions shown in Table 3. This result, CO was effectively consumed without by-producing H_2, indicates that this catalytic reduction did not proceed by the reaction of aromatic nitro compounds and the hydrogen gas that was formed by the WGSR.

A different reaction pathway will be considered from the above results; 9) further studies are now under investigation.

The author wish to express their grateful acknowledgement to Dr. G. Suzukamo, Mr. M. Ishino, and Mr. M. Hazama (Sumitomo Chemical Co. Ltd.) for helpful discussions throughout this research. Prof. Y. Saito (The University of Tokyo) and Prof. A. Miyashita (Saitama University) are also acknowledged for their helpful comments.

References

1) For example (Review), R. M. Laine and E. J. Crawford, J. Mol. Catal., 44, 357 (1988); P. C. Ford and A. Rokicki, Adv. Organomet. Chem., 28, 139 (1988).
2) For example (Review), P. Escaffre, A. Thorez, and P. Kalck, J. Mol. Catal., 33, 87 (1985); Y. Sugi, Shokubai(catalyst), 25, 464 (1983).
3) For example using Ru catalysts, a) K. Cann, T. Cole, W. Slegeir, and R.

Petit, J. Am. Chem. Soc., 100, 3969 (1978); b) H. Alper and R. Amaratunga, Tetrahedron Lett., 21, 2603 (1980); c) T. Okano, K. Fujiwara, H. Konishi, and J. Kiji, Chem. Lett., 1984, 1083; d) E. Alessio, G. Zassinovich, and G. Mestroni, J. Mol. Catal., 18, 113 (1983).

4) We recently found other new catalyst systems which show not only high catalytic activities but also markedly high selectivities of nitro-group for this reduction under the mild conditions at room temperature (25°C) and 1 atm of CO in the presence of aqueous 5 M NaOH solution: K. Nomura, M. Ishino, and M. Hazama, J. Mol. Catal., 65, L5 (1991); 66, L1, L11, L19 (1991); Bull. Chem. Soc., Jpn., in press.

5) It was already known that an excess amount of aqueous NMe_3 solution added $Ru_3(CO)_{12}$ in THF also exhibited the catalytic activity for the $PhNO_2$ reduction,[3a)] however in this case, significant amount of dihydrogen (52% in the gas phase at the end of the reaction) was by-produced, because this catalyst system also shows an exceptionally high WGSR activity (W. A. R. Slegeir, R. S. Sapienza, and B. Easterling, ACS Symp. Ser., 152, 325 (1981)).

6) Turnovers of 329 mol-cat^{-1} was obtained for the reduction of $PhNO_2$ (10 mmol) using $Ru_3(CO)_{12}$ (0.01 mmol) in 2-methoxyethanol/H_2O (15/5 ml) under CO (20 atm) at 150 °C for 2 h.

7) 1-Nitroanthraquinone was also reduced to afford 1-aminoanthraquinone almost exclusively without reducing C=O bond. Turnovers of 1416 and 1516 (mol-cat^{-1}) were obtained by using diisopropylamine-added, and piperidine-added(molar ratio of amine/Ru were 20 and 3, respectively) $Ru_3(CO)_{12}$ (0.005 mmol) in methanol/H_2O (15/5 ml) under CO (20 atm) at 150 °C for 2 h (1-nitroanthraquinone 10.2 mmol).

8) The similar result was also obtained in the reduction of 1-nitroanthraquinone (10.2 mmol) to produce 1-aminoanthraquinone (yield >99.9%) using $Ru_3(CO)_{12}$ (0.005 mmol)-pyrrolidine (0.015 mmol) catalyst in methanol/H_2O (15/5 ml) under CO (20 atm) at 150 °C for 5 h. After the reaction, the stoichiometric amount of CO_2 (34.2 mmol) and a trace amount of H_2 (0.08 mmol) were obtained.

9) For example, R. A. Sheldon,"Chemicals from Synthesis Gas," D. Reidel Publishing Co. Ltd., Dordrecht, pp.181 (1981); T. Ikariya, Shokubai (Catalyst), 5, 271 (1989).

(Received June 19, 1991)