October, 1984] © 1984 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 57, 2867—2870 (1984) 2867

The Platinum Catalyzed Reduction of Nitroarenes to Aminoarenes with Carbon Monoxide and Water

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(Received January 27, 1984)

Nitroarenes were transformed into the corresponding aminoarenes in high yields at 80 °C with carbon monoxide (an initial pressure 30—60 kg cm^{-2}) and water in the presence of a catalytic amount of a platinum catalyst. The platinum catalyst was combined with tin(IV) chloride, triphenylphosphine and triethylamine. This combination was essential for the high catalytic activity.

The homogeneous water gas shift reaction (WGSR) with transition metal catalysts is of current interest[1] (Eq.1).

$$CO + H_2O \xrightarrow{[cat]} H_2 + CO_2 \qquad (1)$$

The application of WGSR to the reduction of organic compounds such as nitroarenes,[2–7] aldehydes[8,9] and olefins[10] has been widely attempted. In these reductions, iron,[2,8] rhodium[2–5,8,9] and ruthenium[2,6–8] clusters have been mostly employed as effective catalysts. With these catalyst systems, however, reaction temperatures are rather high[2,4,8] or a large amount of the catalyst is required under the mild conditions.[4–6]

Concerning the related platinum-catalyzed reaction, Yoshida *et al.* have reported that WGSR can be catalyzed by platinum(0) phosphine complexes.[11] Eisenberg and co-workers described the reduction of olefins with carbon monoxide and HCl aq in the presence of a platinum complex.[10] They also have reported the platinum-catalyzed WGSR and discussed the mechanism of hydrogen and carbon monoxide evolution.[12] The activities of these platinum catalysts, however, were rather low.

In this paper, we describe the platinum-catalyzed reduction of nitroarenes with carbon monoxide and water.[13] The nitroarenes were converted into the corresponding aminoarenes under mild reaction conditions (Eq. 2).

$$Ar\text{-}NO_2 + 3CO + H_2O \longrightarrow Ar\text{-}NH_2 + 3CO_2 \qquad (2)$$

Results and Discussion

The results of nitrobenzene are listed in Table 1. Nitrobenzene was converted into aniline almost quantitatively with dichlorobis(triphenylphosphine)platinum(II) combined with triethylamine and tin(IV) chloride (Runs 1, 2).

When triethylamine was removed from the catalyst system, the reduction did not take place at all (Run 3). The conversion of nitrobenzene was considerably decreased without tin(IV) chloride or triphenylphosphine (Runs 5, 6). In the absence of water or platinum complex, reduction did not proceed (Runs 7, 8). Thus, for the high activity by the present catalyst system, the presence of triethylamine, tin(IV) chloride, and triphenylphosphine is essential.

The effect of the reaction temperature and the initial carbon monoxide pressure are summarized in Table 2. Nitrobenzene was reduced to aniline almost

TABLE 1. THE PLATINUM-CATALYZED REDUCTION OF NITROBENZENE BY USE OF CARBON MONOXIDE WATER.[a] EFFECTS OF COMPONENTS IN THE CATALYST SYSTEM

Run	$SnCl_4$ /mmol	Et_3N /mmol	Conv.[b] /%	Selectivity to[b] aniline/%
1	2.0	2.0	100	98
2	2.0	1.0	100	97
3	2.0	—	9	0
4	1.0	1.0	88	64
5	—	1.0	53	98
6[c]	2.0	1.0	75	99
7[d]	2.0	1.0	3	0
8[e]	2.0	—	4	0

a) A mixture of nitrobenzene (20 mmol), $[PtCl_2(PPh_3)_2]$ (0.10 mmol; 0.5 mol% based on nitrobenzene used.), $SnCl_4$, Et_3N, H_2O (1 ml), and dioxane (10 ml) was stirred under carbon monoxide (initial pressure of 60 kg cm^{-2}) for 4 h. b) Based on the amount of charged nitrobenzene by GLC. c) $[PtCl_2(PhCN)_2]$ (0.10 mmol) as a platinum complex. d) Without water. e) Without platinum catalyst.

TABLE 2. THE PLATINUM-CATALYZED REDUCTION OF NITROBENZENE WITH CARBON MONOXIDE AND WATER UNDER VARIOUS REACTION CONDITIONS[a]

Run	Reaction Temp/°C	CO Pres. /kg cm^{-2}	Reaction Time/h	Nitrobenzene /mmol	Conv.[b] /%	Selectivity[b] to Aniline/%
2	80	60	4	20	100	97
9	50	60	7	20	83	88
10	20	60	22	20	31	71
11	80	30	4	20	100	91
12	80	15	4	10	58	93
13	80	15	20	10	63	86
14	80	bubbling	14	20	32	41

a) Nitrobenzene: $[PtCl_2(PPh_3)_2]$: $SnCl_4$: Et_3N: H_2O: Dioxane=20:0.10:2.0:1.0:56:118 (molar ratio). b) Determined by GLC.

TABLE 3. EFFECT OF SEVERAL LEWIS ACIDS ON THE REACTION[a)]

Run	$\mathrm{Et_3N}$	Lewis acid	Conv./%	Selectivity/%
2	+	$\mathrm{SnCl_4}$	100	97
15	+	$\mathrm{SnCl_2 \cdot 2H_2O}$	78	87
16	+	$\mathrm{FeCl_3}$	40	78
3	—[b)]	$\mathrm{SnCl_4}$	9	0
17	—	$\mathrm{SnCl_2 \cdot 2H_2O}$	78	100
18[c)]	—	$\mathrm{SnCl_2 \cdot 2H_2O}$	79	95
19	—	$\mathrm{FeCl_3}$	15	93
20	—	$\mathrm{AlCl_3}$	15	0
21	—	$\mathrm{ZnCl_2}$	37	84

a) Nitrobenzene 20 mmol, $[\mathrm{PtCl_2(PPh_3)_2}]$ 0.10 mmol, Lewis acid 2.0 mmol, $\mathrm{Et_3N}$ 1.0 mmol, dioxane 10 ml, carbon monoxide 60 kg cm^{-2} at 80 °C for 4h. b) Without $\mathrm{Et_3N}$. c) Reaction time 8h.

quantitatively at 80 °C (Run 2). Lower temperatures, 50 °C and 20 °C, gave only low conversions of nitrobenzene and low selectivities to aniline (Runs 9, 10). The reaction temperature over 80 °C is desired for the high conversion and the high selectivity. The activity of the catalyst system was also affected by the initial carbon monoxide pressure. A higher pressure (60 kg cm^{-2}) of the initial carbon monoxide was more favorable for the reaction (Run 2). The selectivity to aniline slightly reduced to 91% under 30 kg cm^{-2} of the initial carbon monoxide pressure (Run 11). Under 15 kg cm^{-2} of the initial pressure, the conversion of nitrobenzene was not improved even by prolonging the reaction time to 20 h (Runs 12, 13). The reduction was also sluggish with bubbling carbon monoxide and expelling the resultant carbon dioxide from the reaction system (Run 14).

Tin(IV) chloride played an important role in the present catalyst system. Effects of the presence of Lewis acids as co-catalysts with or without triethylamine are summarized in Table. 3. In the presence of triethylamine, tin(IV) chloride was the most favorable. Tin(II) chloride and iron(III) chloride were less effective (Runs 15, 16). On the other hand, the reaction without triethylamine showed an interesting contrast. Employing tin(IV) chloride, aniline was not obtained at all, as mentioned above. However, employing tin(II) chloride, aniline was produced with 100% selectivity and 78% conversion even without the amine (Run 17), although the conversion was not improved by prolonging the reaction time (Run 18). Other Lewis acids, such as iron(III) chloride, aluminum chloride, and zinc chloride were less effective and the conversion was decreased considerably (Runs 19—21).

TABLE 4. REDUCTION OF VARIOUS NITROARENES WITH CARBON MONOXIDE AND WATER[a)]

Run	Nitroarene	Conv./%[b)]	Selectivity to[b)] *aminoarene*
22	4-Methylnitrobenzene	89	80(79)
23[c)]	4-Methylnitrobenzene	100	100
24	4-Chloronitrobenzene	95	94
25[d)]	4-Chloronitrobenzene	96	99(98)
26	3-Methoxynitrobenzene	100	96(95)
27	2-Methylnitrobenzene	87	64
28	2-Methoxynitrobenzene	100	32

a) Nitroarene (20 mmol), $[\mathrm{PtCl_2(PPh_3)_2}]$ (0.10 mmol), $\mathrm{SnCl_4}$ (2.0 mmol), $\mathrm{Et_3N}$ (1.0 mmol), $\mathrm{H_2O}$ (1.0 ml), Dioxane (10 mmol), CO(initial 60 kg cm^{-2} at r.t.)for 4h. b) By GLC, figures in parentheses were determined based on the isolated products. c) $\mathrm{H_2O}$ (0.5 ml). d) at 100 °C.

Various nitroarenes could be converted to the corresponding aminoarenes by this procedure (Table 4). 4-Methylaniline was obtained from 1-methyl-4-nitrobenzene in 71% yield (80% selectivity and 89% conversion) (Run 22). The yield of the product was improved to 100% in the presence of less water (Run 23). 1-Chloro-4-nitrobenzene was converted to 4-chloroaniline in 89% yield (94% selectivity and 95% conversion) at 80 °C (Run 24). The yield increased to 95% (99% selectivity and 96% conversion) by elevating the reaction temperature to 100 °C (Run 25). 3-Methoxyaniline was reduced to 3-methoxyaniline in high yield (Run 26). However, for ortho-substituted nitroarenes, the selectivities to the corresponding aminoarenes were low (Runs 27, 28). The steric effect of the ortho-substituents would cause these low selectivities.

After the reaction, analysis of the gas phase by gas chromatography revealed that only carbon dioxide was produced. Furthermore, a control experiment showed that the present catalyst system could not catalyze the WGSR.14) These observations clearly indicated that the nitroarenes were not reduced to aminoarenes by the hydrogen produced by the WGSR (Eq. 1). In fact, aniline was obtained from nitrobenzene only in 34% yield with the same catalyst system under 60 kg cm^{-2} of hydrogen pressure in place of carbon monoxide and water. This result indicates that carbon monoxide and water is a more effective reductant than hydrogen with the present catalyst system.

Other substrates such as 1-nitropropane, 2-ethyl-2-hexenal, phenylacetylene and diphenylacetylene were not reduced by this procedure. The competitive reduction of nitrobenzene and diphenylacetylene by this procedure15) gave only aniline as the reaction product in 88% selectivity and 80% conversion, while diphenylacetylene was recovered quantitatively. Thus, by the present reaction, the nitroarenes appeared to be reduced chemoselectively. This chemoselectivity is an outstanding feature which was not seen in the previous studies.2—9)

A possible route for the present reaction is as follows. The nitroarenes is deoxygenated with carbon monoxide to an arylnitrene intermediate (Eq. 3). The carbonylation of the nitrene intermediate successively occurs and generates the phenyl isocyanate intermediate (Eq. 4). Iqbal16) has reported the transition metal catalyzed deoxygenation of nitroarenes with carbon monoxide and proposed the nitrene intermediate for the reaction. Bennett *et al.*17) and Collman *et al.*18) have reported the formation of phenyl isocyanate from phenyl azide under carbon monoxide pressure and Bennett *et al.* have suggested that arylnitrene was the reaction intermediate. Furthermore, we have recently reported that the present platinum catalyst system catalyzed the reductive carbonylation of nitroarenes in ethanol and the corresponding ethyl phenylcarbamates were obtained in high yield19) (Eq. 6). We have proposed the arylnitrene and phenyl isocyanate as key intermediates in that reaction. Although that reaction required the elevated reaction temperature (at 180 °C), we recently found that the reaction temperature can be lowered to 150 °C by employing 1 equiv ethanol in benzene.[20] In the present reduction of nitroarenes, we propose the phenyl isocyanate as a key intermediate as mentioned above (Eq. 4). The phenyl isocyanate can react with water to give phenylcarbamic acid which easily decarboxylates to aminoarene (Eq. 5). Tarakanov *et al.* have reported a phenylcarbamic acid intermediate in the reaction of phenyl isocyanate and water.[21] In this reaction, nitroarenes were chemoselectively reduced to aminoarene. This chemoselectivity must be originated in the reaction pathway including the phenylcarbamic acid intermediate.

$$\text{Ar–NO}_2 + 2\text{CO} \longrightarrow \text{Ar–N:} + 2\text{CO}_2 \qquad (3)$$

$$\text{Ar–N:} + \text{CO} \longrightarrow \text{Ar–NCO} \qquad (4)$$

$$\text{Ar–NCO} + \text{H}_2\text{O} \longrightarrow [\text{Ar–NHCOOH}] \xrightarrow{-\text{CO}_2} \text{Ar–NH}_2 \qquad (5)$$

$$\text{Ar–NO}_2 \xrightarrow{[\text{Pt}]} [\text{Ar–NCO}] \xrightarrow{\text{ROH}} \text{Ar–NHCOOR} \qquad (6)$$

There is another possible route, in which the nitrene intermediate abstracts hydrogen from the solvent or other hydrogen source.[22] As indicated by Run 7 (Table 1), the aminoarene was not obtained at all in the absence of water. This result clearly shows that water is the only possible hydrogen source. However, there is no example that nitrene intermediate abstract hydrogen from water, although it is well known that hydrocarbon solvents are good hydrogen donors.[22] Therefore, it is rather hard to accept that the aminoarenes were generated *via* the nitrene intermediate by hydrogen abstraction from water.

In this reaction, characterization of the active catalyst species was not done. Several studies have indicated that Lewis acid promotes migratory insertion of coordinated carbon monoxide to a carbon–metal bond.[23] In the present reaction, tin(IV) chloride may be operative in promoting the insertion of carbon monoxide into a nitrogen–metal bond to generate the phenyl isocyanate intermediate (Eq. 4).

Experimental

Materials. The reagents employed in this study were purified by distillation or recrystallization before use. Carbon monoxide (>99.9%) was used without further purification. Platinum complexes were prepared by the methods in the literature.[24,25]

General Procedure. A 100 ml stainless steel autoclave (Nitto Koatsu SUS 316) equipped with a magnetically driven stirrer was used. A glass liner was set in the autoclave. The reagents were charged in the glass liner in the following order: dioxane (10 ml), water (1 ml), nitroarene (20 mmol), triethylamine (0.14 ml, 1.0 mmol), $PtCl_2(PPh_3)_2$ (79 mg, 0.10 mmol) and $SnCl_4$ (0.24 ml, 2.0 mmol). After sealing and flushing with carbon monoxide, the reactor was pressurized with carbon monoxide to 60 kg cm^{-2} at r.t. The autoclave was heated to 80 °C in 10 min and then held at this temperature for 4 h. The reaction was terminated by rapid cooling and the autoclave was discharged. The resultant clear brown solution was analyzed with GLC.

Product Isolation. The solvent, dioxane, was evapolated off from the reaction mixture and benzene (20 ml) was added. The benzene solution was shaken with 10% HCl aq and the benzene layer was discarded. Then the aqueous layer was neutralized with 20% NaOH aq and extracted with benzene (20 ml). After filtering the whole mixture, the oil layer was separated and dried. Evaporation of benzene from the solution give a pure aminoarene.

Analytical Procedure. The GLC analyses were performed on Shimadzu GC-3BT (with thermal conductivity detector) or GC-4CM (with flame ionization detector) with columns (3 mmϕ×3 m) packed with Versamide 900 (10% on Neopak 1A 60—80 mesh), PEG 20 M TPA (10% on Chromosorb W AW 60—80 mesh) or Apieson Grease L (5% on Neopak 1A). The conversion of the substrate and the selectivity to the product were determined by the internal standard method with naphthalene according to the calibration curve obtained for each sample. The analysis of gas phase was performed on Shimadzu GC-3BT with a column (3 mm ϕ×3 m) packed with Active Carbon 60—80 mesh.

The identification of the products was confirmed by comparing the spectral data (^{13}C-, ^{1}H-NMR and IR spectra) with those of the authentic samples.

The ^{13}C- and ^{1}H-NMR spectra were recorded 25.05 MHz and 100 MHz with a JEOL JNM FX 100 spectrometer. The IR spectra were measured on a Hitachi model 215 grating spectrometer.

Reduction under Hydrogen Pressure. Nitrobenzene (20 mmol) was reduced in the presence of the platinum catalyst system ($PtCl_2(PPh_3)_2$ 0.10 mmol; Et_3N 1.0 mmol; $SnCl_4$ 2.0 mmol) in dioxane (10 ml) under hydrogen pressure (initial pressure 60 kg cm^{-2} at r.t.) at 80 °C for 4 h. After the reaction, GLC analysis indicated that the conversion of nitrobenzene was 39% and the selectivity to aniline was 87% (yield 34%).

Synthesis of Ethyl Phenylcarbamate. A mixture of nitrobenzene (20 mmol), ethanol (20 mmol), $PtCl_2(PPh_3)_2$ (0.20 mmol), $SnCl_4$ (2.0 mmol), Et_3N (3.6 mmol) and benzene (18.5 ml) was stirred under carbon monoxide pressure (initial 60 kg cm^{-2}) at 150 °C for 4 h. The GLC analysis of the reaction mixture showed that ethyl phenylcarbamate was obtained in 70% yield (100% conversion).

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14) A mixture of [$PtCl_2(PPh_3)_2$] (0.10 mmol), $SnCl_4$ (2.0 mmol), triethylamine (1.0 mmol) and water (1.0 ml) was stirred in dioxane (10 ml) under carbon monoxide pressure (initial 60 kg cm^{-2} at r.t.) at 80 °C for 4 h. After the reaction, GC analysis of gas phase showed that no hydrogen and no carbon dioxide were produced.

15) A mixture of nitrobenzene (20 mmol), diphenylacetylene (10 mmol), [$PtCl_2(Ph_3)_2$] (0.10 mmol), $SnCl_4$ (2.0 mmol), triethylamine (1.0 mmol) and water (1.0 ml) was stirred in dioxane (10 ml) under carbon monoxide pressure (initial 60 k cm^{-2} at r.t.) at 80 °C for 4 h.

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