



Selective formation of aromatic amines by selenium-catalyzed reduction of aromatic nitro compounds with CO/H₂O under atmospheric pressure

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Abstract

An efficient method for the catalytic reduction of aromatic nitro compounds to the corresponding aromatic amines is reported. In the presence of selenium as a catalyst, the aromatic nitro compounds are quantitatively reduced by CO/H₂O to form the corresponding amines under atmospheric pressure. The reduction occurs in high selectivity regardless of other reducible functionalities present on the aromatic ring. There exists a phase transfer process of the catalyst selenium in the reaction.

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1. Introduction

Aromatic amines are of significant industrial importance, because they are widely used as the intermediates for synthesis of dyes, pharmaceuticals and agrochemicals [1]. The reduction of aromatic nitro compounds is one of the most common methods for preparing the corresponding aromatic amines. Two methods for reducing the aromatic nitro compounds are used in industry: catalytic hydrogenation [2] and stoichiometric reduction reaction [3]. The catalytic hydrogenation is a clean and convenient method for producing amine in high yield. However, the selective reduction of aromatic nitro compounds with sensitive functional groups, e.g., carbonyl, cyano, chloro, and alkenic groups, is often difficult for catalytic hydrogenation to attain, because these sensitive functionalities are reduced faster with hydrogen than the nitro group [4]. In this case, hydrogen sulfide or variations of this reagents [5] or iron [6] are commonly used, but large amounts of waste are produced.

The reduction of aromatic nitro compounds to the corresponding aromatic amines by use of CO/H₂O as a hydrogen source exhibits high chemoselectivity and is of great industrial potential, especially when a cheap catalytic sys-

tem can be employed. Most catalysts used in such reductions are composed of transitional metals such as Ru, Rh, Pd, etc. [7,8]. Selenium is a cheap catalyst, which is usually used for carbonylation [9–12]. In 1980, Sonoda and co-workers [13] reported selenium-catalyzed reduction of some aromatic nitro compounds to the corresponding amines by using CO/H₂O under high pressure. In their procedure the presence of triethylamine (Et₃N) is essential for the reduction. We have reported that even by using the inorganic salt sodium acetate (NaOAc) as a co-catalyst the high yield can be obtained in the reduction [14]. But the high pressure of CO make it difficult to apply in industry.

Herein we report selenium-catalyzed reduction of aromatic nitro compounds with carbon monoxide and water using the inorganic salt, sodium acetate, as a co-catalyst to give the corresponding amines in the solvent of dimethylformamide (DMF) under atmospheric pressure.

2. Experimental

Carbon monoxide (99.9%) was dried by zeolite 5A. Elemental selenium (99.999%), substrates, bases and solvents were used as purchased.

A typical reaction procedure is described as follows: The reduction was carried out in a 100 ml three-necked flask fitted with a gas inlet tube, a condensator and a magnetic

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stirring bar. Substrates, water, selenium powder, anhydrous NaOAc and solvent (DMF) were placed in the flask. CO was introduced into the flask and the mixture was heated to 96 °C with vigorous stirring. When the reaction was complete, the mixture was cooled to room temperature and CO bubbling was stopped. Then air was introduced into the reaction mixture to precipitate selenium. After filtration of selenium, the filtrate was concentrated and dried over anhydrous magnesium sulfate and analyzed.

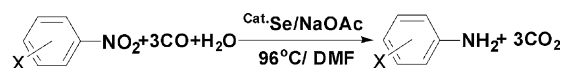
The product was identified by GC–MS (GC-17A-QP-5000MSD) and the spectra obtained were compared with the standard spectra. The amounts of products were determined by GC (HP-4890D) using *n*-C₁₀H₂₂ as an internal standard.

3. Results and discussion

3.1. Selective reduction of aromatic nitro compounds

Representative results are shown in Table 1. Under the conditions employed, no aromatic ureas were found in the product, although ureas are the main by-products in the selenium-catalyzed reduction under the high pressure of CO [13]. Aromatic amines were the only products in the reduction of aromatic nitro compounds. The product selectivities were nearly one hundred percent for all substrates. The electronic effects of substituents in aromatic nitro compounds are obvious. When the electron withdrawing substituents (such as chloro and acetyl) are in the *ortho* and *para* positions where the groups can resonance with the nitro group, these reactions are difficult (entries 4 and 6 in Table 1) or slow (entry 10 in Table 1), owing to the electron withdrawing character of substituents. This indicates that the nitro group receive significant electrons from the conjugated system. Perhaps for the same reason the reduction of aliphatic nitro compounds (such as nitroethane) is difficult under the

present reaction conditions. When the electron withdrawing substituents are in *meta* position and electron releasing substituents do not influence the reaction (entries 1–3, 5, 7–9 and 11 in Table 1), however, the steric effect of alkyl groups is observed, but not strong (entry 1 in Table 1). Except the nitro group, other sensitive functional groups, e.g., carbonyl and chloro groups, cannot be reduced at all (entries 5 and 11 in Table 1).



3.2. The effect of solvents

Why is the nitro group reduced so well by CO/H₂O under mild conditions? We think that the selection of solvents is of great importance. The effect of different solvents on the reaction is shown in Table 2. As can be seen from these data, polar aprotic solvents are essential (entries 1 and 2 in Table 2). First, these polar aprotic solvents can dissolve water and substrates to form a homogeneous system. Secondly, polar aprotic solvents are suitable for the formation of active intermediate. In the experiments, with the blowing of carbon monoxide, selenium can dissolve quickly in the polar aprotic solvents (such as DMF) even in the absence of bases. This process is impossible in the less polar solvents. Even in the presence of Et₃N the process is slow in nonpolar solvents. This indicates that the polar aprotic solvents are favorable for the formation of carbonyl selenide (SeCO) and promote the nucleophilic attack of water to generate selenane (H₂Se or its anions, i.e., HSe⁻), which is regarded as the active intermediate in the Se/CO/H₂O reducing system [13].

With the increase in water, the rate of reaction decreases (entries 2, 7, 8 and 9 in Table 2). In contrast, with the increase in DMF, the rate of reaction increase (entries 2, 10, and 11 in Table 2). When the volume of water is more than the one-third volume of the DMF in the solvent, the reaction is slow (entry 10 in Table 2). Water is not only a reactant but also a solvent. These indicate that the increase in the ratio of water destroys the aprotic character of the solvent. So the formation of active intermediates is difficult and causes the rate of reduction to decrease.

3.3. The effect of bases

The influences of different bases as co-catalysts on the reduction are shown in Table 3. The medium inorganic bases are favorable for the reduction (entries 1 and 3 in Table 3), while organic bases used for carbonylation reaction [21,22] and reduction under high pressure [13,23] are not suitable for this reaction (entries 4 and 5 in Table 3). The strong inorganic bases are not favorable for the reaction (entry 2 in Table 3), even worse than that without bases (entry 7 in Table 3). Perhaps the medium inorganic bases (such as NaOAc and Na₂CO₃) are fit for the stabilization of selenane (H₂Se or its

Table 1

The selenium-catalyzed reduction of aromatic nitro compounds to the corresponding amines under atmospheric pressure with CO/H₂O^a

Entry	Substrate X	Reaction time (h)	Conversion ^b (%)	Selectivity ^c (%)
1	<i>o</i> -CH ₃	4.4	100	100
2	<i>m</i> -CH ₃	4	100	100
3	<i>p</i> -CH ₃	4	100	100
4	<i>o</i> -Cl	4	0.6	100
5	<i>m</i> -Cl	4	100	100
6	<i>p</i> -Cl	4	3.1	100
7	<i>o</i> -CH(CH ₃) ₂	4.2	100	100
8	<i>m</i> -CH(CH ₃) ₂	4.2	100	100
9	<i>p</i> -CH(CH ₃) ₂	4.2	100	100
10	<i>o</i> -COCH ₃	5.5	100	100
11	<i>m</i> -COCH ₃	4	100	100
12	-H	4	100	100

^a Reaction conditions: substrate, 10 mmol; selenium, 0.4 mmol; DMF, 40 ml; H₂O, 2 ml; 96 °C, NaOAc, 5 mmol.

^b Based on the aromatic nitro compounds.

^c Based on the aromatic amine compounds.

Table 2
The influence of solvents in the nitrobenzene reduction reaction^a

Entry	Solvent	Dielectric constant (20 °C)	The amount of solvent (ml)	The amount of water (ml)	Reaction time (h)	Yield (%)	Selectivity (%)
1	DMSO ^b	48.9 [15]	40	8	4	100	100
2	DMF	36.7 [16]	40	8	4	100	100
3	1,2-Diethoxy-ethane ^c	5.5 [17]	40	8	10	–	–
4	1,4-Dioxane	2.2 [18]	40	8	10	–	–
5	Ethanol ^d	25.7 [19]	40	8	10	–	–
6	Acetone ^e	20.7 [20]	40	8	10	–	–
7	DMF	36.7	40	2	2	100	100
8	DMF	36.7	40	4	2.5	100	100
9	DMF	36.7	40	12	5	100	100
10	DMF	36.7	20	8	9	38	100
11	DMF	36.7	60	8	3	100	100

^a Reaction conditions: nitrobenzene, 10 mmol; selenium, 0.4 mmol; 96 °C; NaOAc, 5 mmol.

^b Dimethyl sulfoxide.

^c At 92 °C.

^d At 78 °C.

^e At 56 °C.

anions, i.e., HSe⁻) and increase the concentration of it in the reaction mixture, while the organic bases (such as Et₃N) are favorable for the formation of carbonyl selenide (SeCO). Therefore the mixture of NaOAc and Et₃N used together is the best (entry 8 in Table 3).

3.4. The effect of the concentrations of nitrobenzene

The effect of the concentrations of nitrobenzene on its reduction of nitrobenzene under atmospheric pressure is shown in Table 4. It can be seen that the conversion remains quantitative when concentration of nitrobenzene is increased by four times (entries 1–3 in Table 4).

3.5. The phase-transfer function of selenium-catalyzed system

It is interesting that the selenium catalyst can be recycled for use. At the end of catalytic reduction of nitrobenzene,

carbon monoxide bubbling was stopped. Then air was introduced into the flask and the catalyst was precipitated and recovered. The catalytic activities of the recovered catalysts were practically the same as those of the fresh catalyst, indicating the excellent stability of the catalyst (entries 1, 4, and 5 in Table 4). Before the reaction, the selenium catalyst was in the solid state in the selenium-catalyzed system, which is different in phase with the reagents. During the reaction process, selenium reacts with carbon monoxide to form SeCO, which can then dissolve in the solvent to form a homogeneous catalytic system. In the solvent, SeCO reacts with water to form selenane (or its anions), which reduces the nitrobenzenes to anilines and is oxidized to selenium. The selenium catalyst can be separated from the product by simple phase separation. The selenium-catalyzed reduction system has a function of phase-transfer catalysis in the reaction process and enables toxic selenium catalysts to be easily recovered and reused. Thus, there exists a phase transfer phenomenon of catalyst in this catalytic reaction system. Namely, the reaction system changes from heterogeneous

Table 3
The influences of different bases on the nitrobenzene reduction^a

Entry	Base	Conversion ^b (%)	Selectivity ^c (%)
1	NaOAc	80.7	100
2	NaOH	7.2	100
3	Na ₂ CO ₃	66.1	100
4	Et ₃ N	10.5	100
5	DBU ^d	30.2	100
6	Pyridine	46.6	100
7	none	8.9	100
8	NaOAc + Et ₃ N ^e	100	100

^a Reaction conditions: nitrobenzene, 10 mmol; selenium, 0.4 mmol; DMF, 40 ml; H₂O, 8 ml; 86 °C; 4 h; base, 5 mmol.

^b Based on nitrobenzene.

^c Based on aniline.

^d 1,8-Diazabicyclo[5.4.0]undec-7-ene.

^e NaOAc 5 mmol and Et₃N 5 mmol.

Table 4
The reduction of nitrobenzene catalyzed by selenium under atmospheric pressure^a

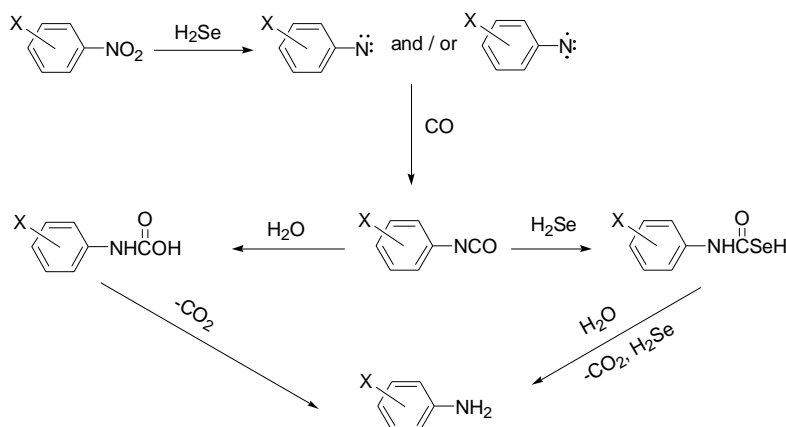
Entry	Cycle ^b	The amount of nitrobenzene (mmol)	Reaction time (h)	Conversion ^c (%)	Selectivity ^d (%)
1	0	5	2	100	100
2	0	10	4	100	100
3	0	20	8	100	100
4	1	10	4	100	100
5	2	10	4	100	100

^a Reaction conditions: selenium, 0.4 mmol; DMF, 40 ml; H₂O, 8 ml; 96 °C; NaOAc, 5 mmol.

^b Number of catalyst recycles.

^c Based on nitrobenzene.

^d Based on aniline.



Scheme 1. A possible reaction pathway for reduction.

to homogeneous and recycles under the heterogeneous system.

3.6. A possible reaction pathway of reduction

Although a detailed study of the reaction pathway has not been conducted, the present reaction can be mechanistically explained by the reaction pathway shown in Scheme 1. Initial deoxygenation of substituted nitrobenzene derivative with selenane (H_2Se or its anions), generated in situ by the reaction of selenium with carbon monoxide and water in the presence of bases, results in an intermediate nitrene and/or nitrenoid which further reaction with carbon monoxide to form isocyanate, followed by nucleophilic attack of water or selenane to give carbamic acid or selenocarbamic acid. Finally the carbamic acid is rapidly decarboxylated or selenocarbamic acid reacts with water to afford the desired aromatic amines derivative and remove of carbon dioxide which was detected by.

4. Conclusions

In summary, the aromatic amines are successfully obtained via the convenient reduction of aromatic nitro compounds with $\text{CO}/\text{H}_2\text{O}$ in DMF under atmospheric pressure catalyzed by selenium with inorganic base as a co-catalyst. This would represent a very convenient reduction protocol to give aromatic amines. The character of phase transfer catalysis is shown in the catalytic process.

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