

CARBONYLATIVE REDUCTION OF NITROPHENOLS TO AMINOPHENOLS*

Vendelin MACHO, Milan KUCERA and Milan KRALIK

Department of Organic Technology,

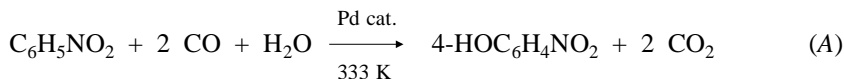
Slovak Technical University, 812 37 Bratislava, The Slovak Republic

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Two- or three-component catalysts composed of (i) sulfur or sulfur compound (H_2S , CS_2 , COS , Na_2S), (ii) basic additive (triethylamine, CH_3ONa , Na_2S), and usually (iii) vanadium(V) compounds (e.g. NH_4VO_3) were found to catalyze efficiently the reaction of $\text{CO} + \text{H}_2\text{O}$ with isomeric nitrophenols to give the corresponding aminophenols. The reaction proceeds smoothly at 398 and 483 K and initial pressure of 7 MPa, and its rate increases from 2- to 4-nitrophenol. The selectivity to aminophenols exceeding 96 per cent was obtained at the water to nitrophenol molar ratio higher than 5. The solvents such as methanol and dioxane ensured better contact of the reactants, which was necessary for achievement of such a high selectivity. The effectiveness of the sulfur components (based on the S content) is expressed by the following sequence: $\text{S} : \text{CS}_2 : \text{Na}_2\text{S} : \text{H}_2\text{S} : \text{COS} = 1 : 1.2 : 2.5 : 10 : 11$. The reaction takes place also under the reduced CO pressure to 0.1 – 0.35 MPa. Formation of side products and mechanism of the reaction are discussed.

As aminophenols are important intermediates for syntheses of pharmaceuticals, antioxidants, dyes, developers, and polymers, the routes to their simple and selective production are investigated. Thus, besides hydrogenation of nitrophenols on supported Group VIII metal catalysts, especially on palladium and platinum¹⁻⁵, and reactions with hydrogen "in statu nascendi", especially important is a two-step synthesis of 4-aminophenol, in which nitrobenzene is first hydrogenated on a heterogeneous catalyst to the intermediate phenylhydroxylamine, followed by the acid-catalyzed rearrangement of the latter to the above product^{5,6}. In the presence of CO and a catalyst formed from Pd(II) salt, triarylphosphine, carbon monoxide, and sulfuric acid, water becomes the hydrogen donor⁷⁻⁹, as shown in Eq. (A).



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However, only 4-aminophenol can be obtained by this way. The other procedures are analyzed in more detail elsewhere⁵. It is worth mentioning that besides hydrogenation of the nitro group on a palladium catalyst, still utilized for reduction of nitrophenols is their reaction with polysulfides, particularly with hydrogen sulfides in alkaline aqueous medium^{10,11}. Although the reaction proceeds at 303 to 383 K, overstoichiometric amounts of the sulfides are required to achieve the nitro group reduction.

In connection with our previous studies of the reductive carbonylation of nitrobenzene^{12,13} and the carbonylative reduction of nitrobenzene to aniline and of dinitrobenzenes to aminonitrobenzenes or diaminobenzenes¹⁴ using a novel catalyst, in the present work we were interested in the selective carbonylative reduction of isomeric nitrophenols to the corresponding aminophenols. Special attention has been paid to the sulfur component of the catalytic system and to the effect of reaction conditions (water to nitrophenol molar ratio and partial carbon monoxide pressure).

EXPERIMENTAL

Chemicals

2-, 3-, and 4-Nitrophenols were commercial chemical purity grade samples (of the higher than 99% purity) as well as the corresponding aminophenol isomers (Lachema Brno, Apolda Buchs, and Aldrich). The other chemicals were of analytical purity grade, and water was redistilled.

Procedures

Reductive carbonylation of individual nitrophenol isomers was carried out in a high pressure stainless steel 250 ml autoclave, equipped with a stirrer (400 rpm) and an electrical heating controlled automatically within ± 2 K. After charging solid and liquid components, the autoclave was closed and then hydrogen sulfide or carbonyl sulfide were introduced by means of the weighed rubber balloon, followed by carbon monoxide pressuring to usually 7 MPa. With stirring, the reaction mixture was heated to 398 or 423 K (ca 30 min). At this temperature the actual temperature and pressure were recorded in 5 – 10 min intervals during 4 or 5 h. Then, stirring was stopped, the autoclave content was cooled, the pressure and temperature were recorded, and the product was weighed. After that, the product was analyzed by GLC (Chrom 5 instrument, flame ionization detector), using 2.4 m long column (3 mm i.d.) packed with 5% silicone elastomer SE 30 on Chromaton N-AWD MCS as the stationary phase. The solvent was *N,N*-dimethylformamide. At feeding point and detector temperature of 423 K, that of the column 453 K, the nitrogen flow rate $40 \text{ cm}^3 \text{ min}^{-1}$ and the hydrogen flow rate $30 \text{ cm}^3 \text{ min}^{-1}$, the components had the following retention times (in min): methanol 0.52, triethylamine 0.62, dimethylformamide 0.67, 2-nitrophenol 2.33, 2-aminophenol 1.50, 3-nitrophenol 3.40, 3-aminophenol 1.73, 4-nitrophenol 4.28, 4-aminophenol 4.00, and methyl *N*-(4-hydroxyphenyl)carbamate 4.03. Experiments were repeated and the data given in the tables are rounded off arithmetic means.

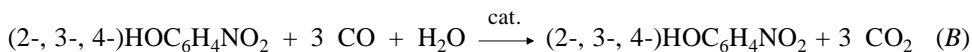
Analysis of Reaction Mixture from Carbonylation Using Water to Nitrophenol Molar Ratio = 1

The reaction product consisted of a liquid and the solid, mostly crystalline portion. The solid (7.0 g) contained 46% 4-aminophenol. Its sample (5 g) was mixed with the same amount of water and 10 g

of methanol and the mixture was refluxed for 10 h. Then, the volatiles were evaporated at 323 K and the solid residue was analyzed. In order to differentiate 4-aminophenol from methyl *N*-(4-hydroxyphenyl)carbamate, GLC conditions were modified (nitrogen flow rate reduced to 30 cm³ min⁻¹, column temperature to 433 K, and after 4-aminophenol elution (3.67 min) increased again to 453 K at which methyl *N*-(4-hydroxyphenyl)carbamate was eluted). The solid residue contained 41% 4-aminophenol and 59% methyl *N*-(4-hydroxyphenyl)carbamate.

RESULTS AND DISCUSSION

As a continuation of our previous work on the reductive carbonylation of nitrobenzene¹³ and the carbonylative reduction of nitro- and dinitrobenzenes¹⁴, in the present work we have applied the catalytic system based on sulfur compounds in a basic medium also on the carbonylative reduction of isomeric nitrophenols (Eq. (B)).



Further data on reaction conditions and results obtained are presented in Table I.

The results show that also nitrophenol isomers can be reduced carbonylatively. In this case the reaction rate under comparable conditions increases from the 2-nitro to 4-nitro derivative. The most effective sulfur compounds, in fact by more than by one order of magnitude when compared to elemental sulfur or carbon disulfide, were proved to be hydrogen sulfide and carbonyl sulfide. This agrees well with our previous observation¹⁴ of a similar effect in the carbonylative reduction of nitrobenzene and dinitrobenzenes. Furthermore, we have proved the applicability of sodium sulfide (and likely also NaHS) which acts both as the donor and the base. The basic medium is a prerequisite for the above catalytic reaction. With regard to the inhibition time of the carbonylative reduction and the course of the pressure decrease, the efficiency of the sulfur components (per mol of the compounds or the amount of the bound sulfur) is following: S : CS₂ : Na₂S : H₂S : COS = 1 : 1.2 : 5 : 10 : 11. We believe that the effect of Na₂S could have achieved that of hydrogen sulfide. The reason of its lower effectiveness is likely the escape of a part of the hydrogen sulfide evolved by hydrolysis of Na₂S · 9 H₂O added into the water present in the autoclave before its sealing and carbon monoxide introduction.

The results support also our assumption that the catalytically active form of the sulfur components is carbonyl sulfide. It seems likely that it is its formation which starts the carbonylative reduction. On the other hand, although ammonium metavanadate acts as a promotor, it is not a prerequisite for the reaction, as it is observed in the case of the reductive carbonylation of nitrobenzene to methyl *N*-phenylcarbamate¹³.

In this connection, the earlier finding by Kondo and coworkers¹⁵ concerning promotion of the reaction $\text{Se} + \text{CO} \xrightarrow{\text{RO}^-} \text{SeCO}$ by an alcoholate anion is of interest. This finding can be utilized also in the synthesis of ureas from aliphatic amines and carbon

monoxide as well as in the preparation of dimethyl carbonate¹⁵ from methanol and carbon monoxide. An analogous situation can be also expected in the case of sulfur and low molecular compounds thereof in a basic medium. Furthermore, Harper¹⁶ reacted a mixture of carbonyl sulfide, nitrobenzene, carbon monoxide, and water to obtain *N,N'*-diphenylurea in the nearly 50% yield.

As proved, the basic medium can be realized also by the use of an ash-free base. In addition, triethylamine used for this purpose distills off easily from the reaction product and can be thus recycled.

Of interest is also the finding that at high excess of water, methanol, and likely also other water-soluble alcohols, can be used as the solvent of nitrophenols. This is made

TABLE I
Effect of catalyst components on carbonylative reduction of nitrophenols to aminophenols (12.5 g of nitrophenol, 12.5 g water, solvent, 7 MPa CO at 298 K, reaction time 4 h, H₂O : nitrophenol molar ratio 7.7)

Nitrophenol	Solvent (mass%) ^a	Catalytic system (mass%) ^a			X ^b , %	S ^b , %
		S-compound	base	NH ₄ VO ₃		
2-NO ₂	dioxane (400)	S (14)	Et ₃ N (12)	0.4	88	98
	dioxane (400)	H ₂ S (4)	Et ₃ N (12)	0.4	68	93
	dioxane (400)	H ₂ S (4)	Et ₃ N (12)	–	57	93
3-NO ₂	dioxane (400)	H ₂ S (4)	Et ₃ N (12)	0.4	99	97
	methanol (100)	H ₂ S (2)	Et ₃ N (12)	0.1	96	96
	methanol (400)	H ₂ S (4)	Et ₃ N (12)	0.1	98	96
	dioxane (400)	CS ₂ (10)	Et ₃ N (12)	0.4	98	97
4-NO ₂	methanol (400)	Na ₂ S ^c (2)	–	0.4	97	99
	dioxane (400)	S (14)	Et ₃ N (12)	0.4	97	98
	dioxane (400)	S (14)	Et ₃ N (1.2)	0.4	99	98
	methanol (400) ^d	H ₂ S (0.8)	Et ₃ N (1.2)	0.4	100	89
	methanol (400)	H ₂ S (0.8)	Et ₃ N (1.2)	0.4	100	89
	methanol (400)	COS (0.8)	Et ₃ N (12)	0.4	100	99
	methanol (400)	COS (0.7)	Et ₃ N (12)	0.4	99	98
	methanol (100) ^e	Na ₂ S ^c (2)	–	0.4	96	98
	methanol (100) ^e	Na ₂ S ^c (2)	–	–	84	90
methanol (100) ^e	Na ₂ S ^c (1)	–	0.4	75	88	

^a With respect to the nitrophenol; ^b X conversion of nitrophenol, S selectivity to aminophenol; ^c Na₂S as the nonahydrate (Na₂S · 9 H₂O); ^d water to 4-nitrophenol molar ratio 1.6; ^e at 398 K.

possible by the fact that alkyl *N*-(hydroxyphenyl)carbamates are not formed, the only products being aminophenols.

Table II presents the results of the carbonylative reduction of 4-nitrophenol at the initial CO pressures 0.35 and 0.40 MPa. In place of usual 12.5 g, the weight amount of the 4-nitro derivative was only 5 g, to ensure the possibility of the complete conversion of the nitrophenol by the present carbon monoxide. The latter was achieved after 5 h, with the selectivity to 4-aminophenol higher than 97 per cent. Also these results indicate that the carbonylative reduction takes place even at the CO partial pressure 0.35 MPa. Furthermore, the complete 4-nitrophenol conversion under these conditions allows to conclude that the reduction proceeds even at the lower CO pressure of around 0.1 MPa. Obviously, even though at the slower but still measurable rate, the carbonylative reduction could proceed in the presence of the above catalyst already at the CO partial pressure equaling to or being higher than 0.1 MPa.

With regard to the competition reactions (C) and (D) and likely due to the higher reactivity of the intermediate nitrene¹² with water than with methanol, even at the water to 4-nitrobenzene molar ratio equaling to 1, the selectivity to 4-aminophenol equals to

TABLE II

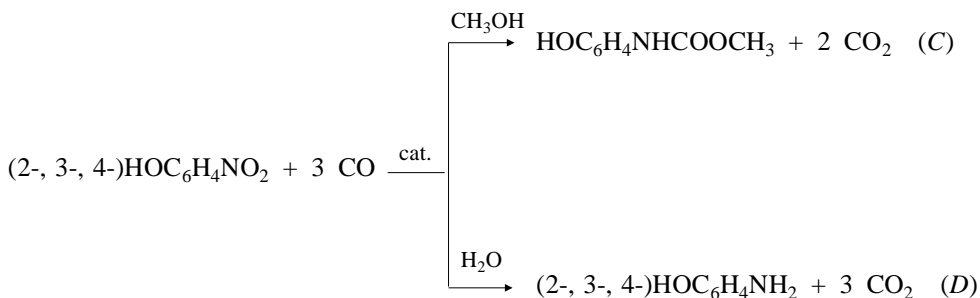
Effect of initial CO pressure (in MPa) and water to nitrophenol molar ratio (*Y*) on carbonylative reduction of 4-nitrophenol (temperature 398 K, 12.5 g 4-nitrophenol, 25 g solvent, *x* g water, 0.0125 g NH₄VO₃, reaction time 5 h)

CO pressure	<i>Y</i>	Solvent	Catalytic system (mass%)		<i>X</i> ^a , %	<i>S</i> ^a , %
			S-compound	base		
0.35 ^b	12.7	methanol	CS ₂ (10)	CH ₃ ONa (10)	100	98
0.40 ^b	12.7	dioxane	S (10)	Et ₃ N (10)	100	97
0.35 ^b	7.7	methanol	H ₂ S (1)	Et ₃ N (10)	100	98
0.35 ^b	7.7	dioxane	S (10)	Et ₃ N (10)	100	97
7	7.7	dioxane	H ₂ S (1)	Et ₃ N (10)	100	99
7	7.7	dioxane	H ₂ S (1)	Et ₃ N (5)	99	99
7	5	methanol	CS ₂ (10)	Et ₃ N (10)	99	97
7	3	methanol	CS ₂ (10)	Et ₃ N (10)	100	91
7	2	methanol	CS ₂ (10)	Et ₃ N (10)	99	88
7	1	methanol	CS ₂ (10)	Et ₃ N (10)	100	74
7	–	methanol	CS ₂ (10)	Et ₃ N (10)	100	0.2 ^d

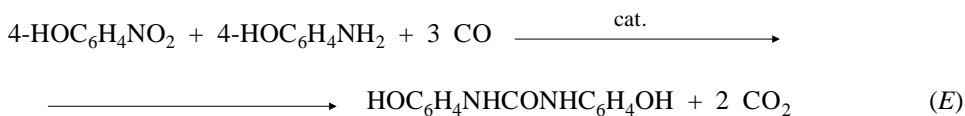
^a For *X* and *S* see footnote^a in Table I; ^b batch contained only 5 g of 4-nitrophenol; ^c at 423 K;

^d the selectivity to methyl *N*-(4-hydroxyphenyl)carbamate was 81 per cent.

73.4 per cent. To achieve the more than 96% selectivity, the above ratio has to be equal or higher than 5. The side products formed are above all



methyl *N*-(4-hydroxyphenyl)carbamate (Eq. (C)), and to the less extent also the competitive reductive carbonylation of 4-nitrophenol to *N,N'*-bis(4-hydroxyphenyl)urea (Eq. (E)).



However, also other reductive carbonylations (Eqs (F) and (G)) cannot be excluded, although by us their products have not been detected.



In the absence of water, the main reaction is the reductive carbonylation of 4-nitrophenol to methyl *N*-(4-hydroxyphenyl)carbamate (81% selectivity). The other products in this case are likely those formed by Eqs (E) and (F).

The reaction product from the experiment in which water and 4-nitrophenol were used in the molar ratio 1 : 1 was a mixture of liquid and crystalline portion. The liquid phase (27.8 g) contained 69% of a mixture of methanol and triethylamine and 31% of 4-aminophenol. The solid portion (7.0 g) contained 46% of 4-aminophenol. Its further

treatment (for details see Experimental) and GLC analysis showed that the final solid consists of 41% 4-aminophenol and 59% of methyl *N*-(4-hydroxyphenyl)carbamate. This also documents that we deal here with the compounds formed according to Eqs (C) to (E).

Summarizing, the catalytic system described in the present work thus catalyzes not only the reductive carbonylation of nitrobenzene to alkyl *N*-(hydroxyphenyl)carbamates¹³ but also the oxidative carbonylation of aniline to *N,N'*-diphenylurea and methyl *N*-phenylcarbamate¹⁷, carbonylative reduction of nitrobenzene to aniline, and dinitrobenzenes to diaminobenzenes¹⁴ as well as reduction of nitrophenols to aminophenols.

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