

New catalytic system of *N,N'*-diphenylurea synthesis from nitrobenzene, carbon monoxide and water or aniline

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Received 1 September 1995; revised 9 December 1995; accepted 14 December 1995

Abstract

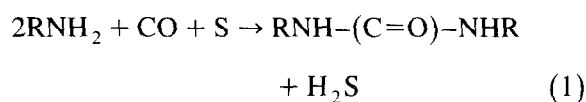
The influence of aniline (PhNH₂) on the reductive carbonylation of nitrobenzene (PhNO₂) by carbon monoxide and an excess of methanol, catalyzed by (w/w % with respect to PhNO₂): sulfur (10), sodium methoxide (2), ammonium metavanadate (0.1), at 423 ± 2 K and starting pressure of CO 13 MPa (298 K) was investigated. Methyl-*N*-phenylcarbamate (MPC) is formed predominantly, via the formation of the intermediate *N,N'*-diphenylurea (DPU) which is subsequently alcoholized by methanol. *N*-Phenylformamide (NPF) is the main by product. In the presence of water, PhNO₂ is carbonylatively reduced to PhNH₂, and DPU is formed by reductive carbonylation from PhNO₂, CO and PhNH₂. Thus, DPU can be obtained directly from PhNO₂ in a one-step process. If an excess of PhNH₂ is applied, the conversion of PhNO₂ is practically total, a small amount of NPF is formed as in the case of the reductive carbonylation of PhNO₂ in the presence of methanol. The efficiency of other tested sulfur compounds increases in the sequence: S < CS₂ ≪ Na₂S < H₂S < COS. The dominant effect of sulfur components, a basic environment as well as the promotive effect of vanadium(V) compounds on the reductive carbonylation and carbonylative reduction of nitrocompounds has been confirmed.

Keywords: *N,N'*-Diphenylurea; Nitrobenzene; Aniline; Methyl-*N*-phenyl carbamate; Sulfur compounds; Vanadium; Reduction; Carbonylation

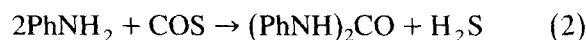
1. Introduction

N,N'-Diphenylurea (DPU) is seeing growing interest in the field of chemical technology, e.g. it is a promising intermediate for the production of isocyanates by phosgene-free routes [1]. DPU can be prepared by various well known processes [2,3]. The formation of dialkylureas and diarylureas from alkylamines reacting with stoi-

chiometric amounts of sulfur and carbon monoxide at approx. 100°C is reported [4]:



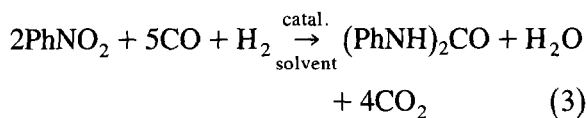
Similarly, DPU is formed from stoichiometric amounts of aniline and carbon oxysulfide [5]:



Furthermore, the 50% yield of DPU, calculated with respect to COS, was achieved upon

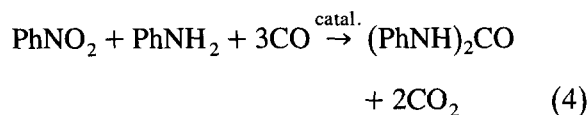
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reacting PhNO_2 , COS and water in the presence of bases and high pressures [6]. Work [7,8] carried out on the reaction of PhNO_2 , CO and water catalyzed by selenium or on compounds of ruthenium and rhenium using hydrogen instead of water.



They reported a 66.3% yield of DPU, but investigation of the effects of a basic environment are not mentioned.

In our previous work [3], similarly to observations of Dieck et al. [9], the formation of DPU from PhNO_2 , CO and H_2 , or alternatively water, with palladium and Lewis acids as catalysts, in a one-step process has been described. A remarkable series of papers [10] dealing with mainly palladium catalyzed synthesis of DPU from PhNO_2 , PhNH_2 and CO appeared in a connection with a previous report [3]. The stoichiometry of this synthesis is expressed by:



The results mentioned above, together with an interesting paper devoted to the oxidative carbonylation of aniline by carbon monoxide and oxygen, to give DPU in the presence of selenium, tellurium or sulfur as catalyst [11–14], particularly in the form of low molar weight compounds [15–19], have given rise to speculation about possible routes of preparation of DPU, and other diarylureas. Details of the synthesis of DPU from PhNO_2 , CO and water or aniline, using a new catalytic system are presented here.

2. Experimental

All organic and inorganic chemicals were of analytical grade. PhNO_2 and PhNH_2 were purified by vacuum distillation in an inert atmo-

sphere prior to use. The content of water (w/w %) was 0.026% in PhNO_2 , 0.046% in PhNH_2 and 0.11% in methanol. The carbon monoxide utilized in experiments contained impurities (vol. %): hydrogen: 1.2, nitrogen: 0.6, oxygen: 0.1, COS: 8.7×10^{-6} , H_2S : 7.5×10^{-4} , CS_2 : 5×10^{-6} . The determination of sulfur compounds in the supply of CO was very important for evaluation of the contribution of these species to the activity of the new catalytic system.

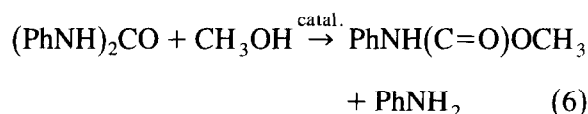
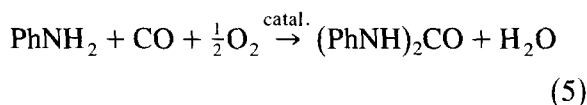
The reductive carbonylation was carried out in a 500 ml stainless steel high pressure reactor system rotating at 240 rpm with heating controlled to ± 2 K. Air present in the reactor was not removed before addition of the reactants. The initial pressure of CO was 13 MPa/298 K.

Reaction mixture was analyzed by GC and HPLC, following procedures described in detail in our previous work [15–19]. Sulfur compounds in the supply of CO were analyzed by the GC instrument MCH-120 using the Teflon column (length 1800 mm, inner diameter 3.2 mm, Chromosil 330 as stationary phase) operated at 40°C, equipped with a flame photometric detector. Nitrogen as carrying gas, hydrogen and air as auxiliary gases were utilized.

3. Results and discussion

With regard to the formation of PhNH_2 (even that in a negligible amount) as the by product of reductive carbonylation of PhNO_2 in the presence of methanol to MPC [15–19], the influence of the PhNO_2 to PhNH_2 molar ratio in the reductive carbonylation of PhNO_2 , was our main interest. The results are summarized in Table 1. When only PhNO_2 was treated (the run 1), the 96% selectivity to MPC and non-formation of NPF, with total conversion of PhNO_2 , was achieved. PhNH_2 on its own (the run 2) exhibited the selectivities of 56% to MPC, 25% to DPU and 19% to NPF, with 21% conversion of PhNH_2 being achieved after 4 h. In the latter case, the partial oxidative carbonylation of PhNH_2 [15] consuming oxygen from CO and

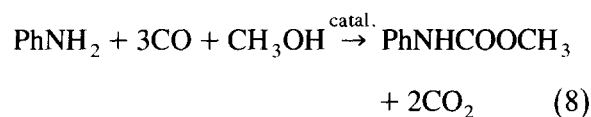
from the air present in the reactor (the volume of the reactor was not outgassed before the experiment) is supposed to take place, as outlined in Eqs. (5) and (6).



PhNH_2 can also react with CO, obeying the reaction:



All other experiments of the reductive carbonylation of PhNO_2 in the presence of methanol and various amounts of PhNH_2 showed reaction (4) to be dominant. The reaction of PhNH_2 , CO and CH_3OH (formation of MPC, Eq. (8)) proceeds significantly slower than reaction (4), probably, due to the lower basicity of methanol than PhNH_2 .



The dominance of reaction (4) has been also

proved by results of analysis of the ‘pure’ reaction time t_p as a function of the amount of PhNO_2 in the mixture of PhNO_2 with the PhNH_2 at the start of reaction. The ‘pure’ reaction time was determined from a decrease of the total pressure after recalculation the consumption of CO to standard conditions, under assumption of the total conversion of PhNO_2 with respect to the stoichiometry of Eqs. (4) and (8). The concave parabolic shape of the curve in Fig. 1 illustrates a positive effect of increasing amount of PhNH_2 on the reaction rate.

Experiments carried out for longer than t_p showed increased amounts of MPC formed by alcoholysis of DPU by CH_3OH (6). However, higher amounts of PhNH_2 in the reaction mixture increases the extent of reaction (7) and consequently, the selectivity to NPF formation is increased (runs 4–10, Table 1). Due to the calculation of selectivities with respect to starting amount of MPC, experiments with low molar ratios ‘ $\text{mr} = \text{PhNO}_2:\text{PhNH}_2$ ’ allowed selectivities higher than 100% to be achieved, e.g. 112% for ‘ $\text{mr} = 1:7$ ’ (Table 1, run 10). This result again confirms the course of oxidative carbonylation of PhNH_2 (7). Finally, we cannot exclude formation of DPU via reactions (1) and (2), though we were not successful in finding

Table 1
The influence of $\text{PhNO}_2:\text{PhNH}_2$ molar ratio on the reductive carbonylation ^a of PhNO_2 in the presence of methanol

Run	Molar ratio $\text{PhNO}_2:\text{PhNH}_2$	Conversion PhNO_2	Selectivity ^b (%)			Selectivity PhNH_2 to NPF (%)
			MPC ^c	PhNH_2	DPU ^d	
1	1:0	100	96	3	–	0
2	0:1	21 ^e	56 ^e	–	25 ^e	19 ^e
3	1:0.5	100	83	1	16	6
4	1:1	100	85	–	14	2
5	1:2	100	87	–	13	7
6	1:3	100	86	–	13	6
7	1:4	100	85	–	15	13
8	1:5	100	87	–	13	18
9	1:6	100	100	–	2	18
10	1:7	100	112	–	0.5	20

^a Conditions: reactor 500 cm³, $\text{PhNO}_2 + \text{PhNH}_2 = 0.4$ mol, methanol 3 mol, sulfur 0.15 mol, sodium methoxide 0.018 mol, sodium metavanadate 2.3×10^{-5} mol, 4 h, 423 K, 13 MPa (298 K) at the start.

^b Selectivity calculated to the conversion of PhNO_2 .

^c Methyl-*N*-phenyl carbamate.

^d *N,N'*-diphenylurea.

^e Selectivity to the conversion of PhNH_2 .

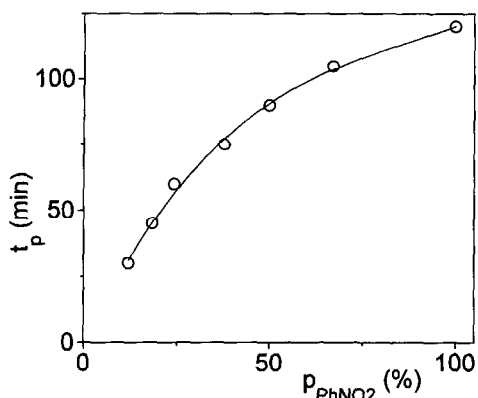


Fig. 1. Dependence of the pure reaction time (t_p) of reductive carbonylation of PhNO_2 , on the mole fraction of PhNO_2 (p_{PhNO_2}) in the mixture of PhNO_2 and PhNH_2 in the starting reaction mixture. Conditions are given in the notes to Table 1.

convincing evidence of this. An excess of methanol and a sufficiently long reaction time have caused the extensive alcoholysis of DPU

to MPC and PhNH_2 (6) which is shown by all the runs in Table 1.

Next we investigated the effects of modifiers of the catalytic system, on the formation of DPU. This was both to utilize the intermediate PhNH_2 for the preparation of DPU (our previous observations [3]), and the low sum of selectivities achieved in the carbonylative reduction and the reductive carbonylation of nitroaromates to arylamines and methyl-*N*-aryl carbamates [15–18]. Results obtained under certain reaction conditions are listed in Table 2, from which, also, a reproducibility of experiments (the first 3 runs) can be evaluated.

In accord with previous results [16], PhNO_2 is carbonylatively reduced to PhNH_2 in the presence of water.

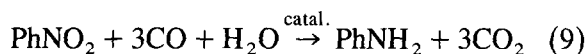


Table 2

Carbonylative reduction ^a of PhNO_2 conjugated with the reductive carbonylation of PhNO_2 and PhNH_2

Run	T (K)	Dioxane ^b (%)	Water ^b (%)	r_{wp} ^c	Catalytic system (%) ^d			x ^e (%)	Selectivity (%) ^f		
					Sulfur compound	Et_3N	Vanadium compound		PhNH_2	DPU	NPF
1	393	—	200	6.85	H_2S (1.2)	8	0.2	53	15	82	1.7
2	393	—	200	6.85	H_2S (1.2)	8	0.2	66	16	82	1.4
3	393	—	200	6.85	H_2S (1.2)	8	0.2	57	13	81	1.6
4	393	—	200	6.85	H_2S (4.8)	8	0.2	54	44	53	1.8
5	413	—	7	0.48	H_2S (2)	6	0.4	37	67	31	1.2
6	413	—	10	0.68	H_2S (2)	6	0.4	52	68	28	1.3
7	413	—	17	1.16	H_2S (2)	6	0.4	62	59	38	1.4
8	413	—	50	3.42	COS (2)	8	0.4	99	38	59	1.0
9	413	—	50	3.42	CS_2 (10)	8	0.4	87	29	70	1.0
10	423	100	3.2	0.22	H_2S (2)	10	0.2	20	75	24	1.0
11	423	100	8	0.55	H_2S (2)	2	0.2	43	61	38	1.0
12	423	100	8	0.55	H_2S (2)	10	0.2	50	44	55	1.0
13	423	100	8	0.55	H_2S (2)	2	0.2	44	57	42	1.0
14	423	100	11.6	0.8	H_2S (4)	4	0.2	52	69	28	1.9
15	423	100	200	6.85	H_2S (4)	4	0.2	94	74	22	2.1
16	423	—	200	6.85	Na_2S (0.97) ^g	—	0.2	35	33	61	2.0
17	423	—	200	6.85	Na_2S (1.46) ^g	—	0.2	37	48	49	2.2
18	423	—	200	6.85	Na_2S (2.9) ^g	—	0.2	48	93	4	2.6
19	423	—	200	6.85	Na_2S (2.9) ^g	2	0.2	97	92	5	2.8

^a Conditions: reactor 500 cm³, PhNO_2 50 g, dioxane, water, components of the catalytic system, 4 h, 423 K, 13 MPa(298 K) at the start.

^b w/w % with respect to PhNO_2 .

^c Molar ratio water: PhNO_2 .

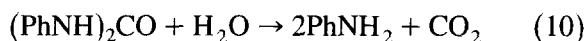
^d w/w % with respect to PhNO_2 . Et_3N : triethylamine, vanadium compound: NH_4VO_3 .

^e Conversion of PhNO_2 . (w/w % to PhNO_2).

^f With respect to the conversion of PhNO_2 .

^g In the form of $\text{Na}_2\text{S} \cdot 3\text{H}_2\text{O}$, expressed as w/w % to PhNO_2 .

PhNH₂ can react giving NPF (7), but mainly it is consumed in the reductive carbonylation of PhNO₂ to DPU (4). The conversion of PhNO₂ at temperatures from 393 up to 423 K and reaction time 4 h, is relatively low, except for the run in which COS was prepared as the component of the catalytic system prior to the start of the reaction. The positive feature of these runs is the good selectivity to DPU. A polar organic solvent (e.g. dioxane), in addition to better solubility of PhNO₂ in the reaction mixture, also improves the contact of reactants in the individual phases. As a result of these effects, both the rate of reaction and the selectivity to PhNH₂ formation increase. The selectivity to NPF is low because of the formation of NPF by the consequent reaction of PhNH₂ and CO (7) which is slower than the formation of DPU via the reductive carbonylation of PhNO₂ by PhNH₂ and CO (4). Moreover, DPU is hydrolyzed by water:



Also, the hydrolysis of NPF can be supposed:



If reaction (11) proceeds to a significant extent, formic acid generated in the reaction system, can decrease the basicity of a reaction environment, as a result of this, the rate of carbonylative reduction is decreased, or can even stop altogether.

The necessity to have sulfur compounds and a strong basic reaction environment led us to experiments with Na₂S as a component of the catalytic system (Table 2, runs 16–19). Suitability of this component is evident, especially for the carbonylative reduction of nitrobenzene, and likely, other nitroaromates, too. If a polar organic solvent would be applied, an improvement of the reaction rate and particularly the selectivity to DPU is expected. The further improvement of the process can be achieved by utilization of phase transfer components, e.g. similarly like in the case of Et₃N (the comparison of runs 18 and 19 in Table 2, run 8 in Table 3).

On the basis of previous results [15–19], we supposed a proportionality of the behaviour (the reaction rate and selectivities) of reductive carbonylation of PhNO₂ by CO and PhNH₂, to components of the catalytic system. To check

Table 3
Effect of components of the catalytic system on the reductive carbonylation^a of PhNO₂ in the presence of PhNH₂

Run	Sulfur compound	Catalytic system (%) ^b		Conversion (%)		Selectivity ^c (%)	Selectivity ^d to NPF (%)
		basis	NH ₄ VO ₃	PhNO ₂	PhNH ₂		
1	H ₂ S(1.5)	–	–	39	11	84	12
2	H ₂ S(1.5)	–	–	20	7	75	38
3	H ₂ S(4)	–	0.2	69	19	99	10
4	H ₂ S(2)	–	0.2	57	18	99	25
5	–	Et ₃ N(10)	–	24	10	20	65
6	H ₂ S(2)	Et ₃ N(10)	–	50	16	99	27
7	H ₂ S(2)	Et ₃ N(10)	0.2	98	32	94	17
8	H ₂ S(2)	Et ₃ N(10)	0.2	98	29	98	17
9	CS ₂ (2)	Et ₃ N(10)	0.2	99	30	96	32
10	CS ₂ (2)	Et ₃ N(10)	0.2	45	15	86	32
11	H ₂ S(2)	CH ₃ ONa(1)	0.2	27	7	99	13
12	–	CH ₃ ONa(1)	0.2	11	3	99	10

^a Conditions: reactor 500 cm³, PhNO₂ 50 g (0.4 mol), PhNH₂ 150 g (1.6 mol), components of the catalytic system, 4 h, 423 ± 2 K, 13 MPa (298 K) at the start.

^b w/w% with respect to PhNO₂, Et₃N: triethylamine.

^c Selectivity of the conversion of PhNO₂ to DPU.

^d Selectivity of the conversion of PhNH₂ to NPF.

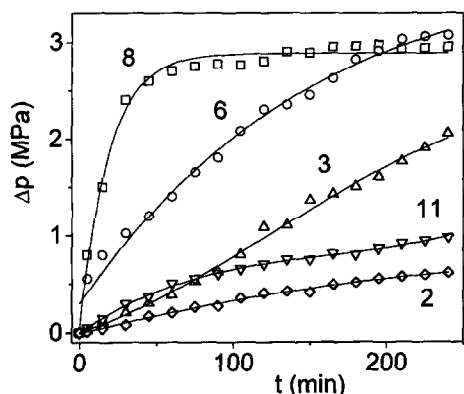


Fig. 2. Effect of composition of the catalytic system on the rate of reductive carbonylation of PhNO_2 by CO and PhNH_2 . Conditions of experiments are given in the notes to Table 3, numbers over curves denote runs as listed in Table 3.

this proportionality, experiments summarized in Table 3 were performed. The molar ratio $\text{PhNH}_2:\text{PhNO}_2$ was chosen to set to 4 for all these experiments. From the decrease of pressure of CO, an evaluation of the kinetic behaviour was done, to this, Fig. 2 presents some runs corresponding to Table 3.

The highest rate (run 8) was achieved using the catalytic system (w/w % to PhNO_2): H_2S (2), Et_3N (10), NH_4VO_3 (0.2), and the lowest rate is exhibited by the experiment without addition of base and NH_4VO_3 (the run 2). This implies that the basicity of aniline alone is not sufficient for the appropriate rate of the reaction, which is shown by the runs 3 and 4. Exclusion of ammonium metavanadate from the catalytic system also causes a decrease of the reaction rate, like that shown by run 6 in comparison to that of run 8. The promotive effect of ammonium metavanadate is shown by run 3 (a strong base was not involved) in comparison with run 2. This positive effect is also evident from a comparison of runs 3–8 in Table 3. The negative effect of low solubility of a component of the catalytic system on the activity is shown by comparison of the runs with H_2S (totally soluble), with the runs where CS_2 (partially soluble) was applied.

If a three or more times excess of PhNH_2 is

applied in the starting reaction mixture, the relatively high selectivity to NPF which is formed through the competitive carbonylation (7), can be achieved. As for synthesizing DPU, the best conditions are a pressure of about 10 MPa and a temperature of about 423 K. The 98% selectivity to DPU at 100% conversion of PhNO_2 could be obtained applying the proposed catalytic system. Since the system is not sensitive to common poisons, various sources of unpurified CO, even with a low concentration of CO, can be employed for the reductive carbonylation and carbonylative reduction of organic nitrocompounds on industrial scale. From practical point of view (reaction rate and selectivities to individual products), a good contact between the phases of the reaction system is very important. Proper surface-active components (similarly to Et_3N) can improve the economical features of the process.

The significant influence of sulfur compounds on the rate of reductive carbonylation is illustrated by experiments (runs 5 and 12) in which non-sulfur compounds were added to the reaction system at the start of the reaction and despite their presence, a reasonable reaction rate was observed. Catalytic effects can be attributed to the presence of low amounts of sulfur compounds in CO supplied from a bomb (see Experimental) which once more emphasizes the advantages of the proposed catalytic system for potential industrial applications.

All observations obtained allow us to state the following sequence of the catalytic activity of sulfur compounds: $\text{S} < \text{CS}_2 \ll \text{Na}_2\text{S} < \text{H}_2\text{S} < \text{COS}$. Very likely, COS can be considered to be the main catalytic component, even that COS is a catalytic moiety involved into a catalytic cycle, in a formation of intermediate nitrene by reduction of a nitro group, occurs. Basic environment helps formation of COS substantially [19]. This can be supposed as an analogue to the formation of COSe in the presence of CH_3ONa or Et_3N as catalysts, described by Kondo et al. [12]. The promotive effect of vanadium(V) can be attributed to the assistance of an electron

transfer in the reaction system, in particular, the insertion of CO to the nitrene group, but an effect on the formation of COS from CO and S cannot be excluded definitely.

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