# REDUCTIVE CARBONYLATION OF NITROBENZENE TO N,N-DIETHYL-N′-PHENYLUREA

Vendelin MACHO[a], Milan KRALIK[a], Gabriel LIGAC[a], Eva BOJSOVA[b] and Lorant VOJCEK[a]

[a] *Department of Organic Technology,*
*Slovak Technical University, 812 37 Bratislava, Slovak Republic*
[b] *Research Institute of Petrochemistry,*
*971 04 Prievidza, Slovak Republic*

Reductive carbonylation of nitrobenzene with carbon monoxide and diethylamine at 363–443 K and initial CO pressures 6–17 MPa in the presence of a catalyst consisting of sulfur or a sulfur compound and a vanadium(V) compound in a basic medium yields N,N-diethyl-N′-phenylurea as the main product. Formation of the side products (aniline, N,N′-diphenylurea, and N-phenylformamide) is affected significantly by water admixtures. The efficiency of sulfur components increases in the order: S : $CS_2$ : $H_2S$ : COS = 1 : 1.2 : 5.7 : 8. The presence of the vanadium(V) compound, although not prerequisite, has promoting effect. The selectivity and reaction rate of the carbonylation increases with increasing CO pressure. Water affects negatively above all the selectivity of the reaction (at 0.24 wt.% water in diethylamine, maximum selectivity exceeds 80%, at 1.6 wt.% water it is only ca 60%). The effect of reaction conditions and the course of side reactions is discussed.
**Key words:** Reductive carbonylation; Sulfur compounds as carbonylation catalyst; Ammonium metavanadate as promotor; N,N-Diethyl-N′-phenylurea, synthesis.

N,N-Diethyl-N′-phenylurea (DEPU), an interesting intermediate of pesticide, pharmaceutics and epoxide resins[1] production, can, besides the addition of diethylamine to phenyl isocyanate, be prepared by the reaction of aniline with carbonyl sulfide[2]. Another routes are the reductive carbonylation of nitrobenzene with carbon monoxide and diethylamine in the presence of thioamines as catalysts[3,4] and the reaction of nitrobenzene with carbon monoxide and water or aniline in basic solution of tetrahydrofuran, catalyzed by selenium[5]. Still of the greater interest is the synthesis of N,N-dialkyl-N′-arylureas from nitroaromatic hydrocarbons or mixtures of these compounds with arylamines, dialkylamines and carbon monoxide in the presence of catalytic amounts of sulfur or sulfur compounds and at least one oxovanadium(V) component[6].

As a continuation of the above works and our studies[7–9] on a novel catalytic system for the reductive carbonylation of nitrobenzene with CO and alkanols to alkyl N-phenylcarbamates[7,8], with CO and $H_2O$ to aniline and with nitroaromatic hydrocarbons to arylamines[9], we considered it useful to examine the effect of catalyst components and

other reaction conditions on the reductive carbonylation of nitrobenzene with CO and diethylamine to DEPU (Eq. (*A*)).

$$C_6H_5NO_2 + (C_2H_5)_2NH + 3\ CO \xrightarrow{\text{cat.}} C_6H_5NHCON(C_2H_5)_2 + 2\ CO_2 \quad (A)$$
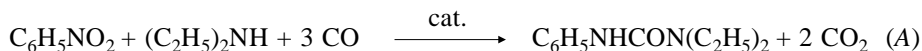
### EXPERIMENTAL

#### Chemicals

Carbon monoxide contained the following admixtures (in vol.%): hydrogen 1.2, nitrogen 0.6, oxygen 0.1, carbonyl sulfide $8.7 . 10^{-6}$, hydrogen sulfide $7.5 . 10^{-4}$, and carbon disulfide $5 . 10^{-6}$. Nitrobenzene, pure, contained 0.046 wt.% water. Diethylamine contained l.6 wt.% water. Its extractive distillation with diethylene glycol as the extractant yielded the sample containing 0.24 wt.% water. The other chemicals were of chemical purity.

#### Procedure

Experiments were carried out in a 500 $cm^3$ stirred (180 rpm) stainless steel autoclave heated electrically. Nitrobenzene, diethylamine, *N*-phenylformamide, and aniline were determined gas chromatographically[7,10,11], and DEPU, *N,N′*-diphenylurea (DPU), and *N*-phenylformamide (NPF) were analyzed by HPLC (Pye Unicam P 4100 with UV VIS 4100 detector) using a $180 \times 3.3$ mm Separon CGC C18 (Tessek Prague) column (particle size 5 µm) under following conditions: detection at the wavelength 25 nm, methanol–water = 1 : 1 (v/v) mobile phase, the direct calibration, *RT* (min) for NPF 4.0, DEPU 7.0, and DPU 10.0.

Some samples were analyzed by GLC on a HP 5880A Hewlett–Packard chromatograph, using PONA capillary column (length 50 m and i.d. 0.21 mm) at 423 K (injection port temperature 523 K, detector temperature 553 K, helium flow rate 0.35 $cm^3\ min^{-1}$ (hydrogen 27 $cm^3\ min^{-1}$ and oxygen 90 $cm^3\ min^{-1}$), splitting ratio 1 : 80. Under these conditions *RT*'s (min) were for $Et_2NH$ 7.34, nonane 9.14, phenyl isocyanate 9.98, aniline 10.14, and for nitrobenzene 12.84.

### RESULTS AND DISCUSSION

Data on the effect of temperature on the course of the reductive carbonylation of nitrobenzene with CO and $Et_2NH$ (Table I) show that the highest initial reaction rate, determined by following pressure decrease in the autoclave during 30 min is achieved at 393–403 K, the nitrobenzene conversion being practically quantitative in 4–5 h. Further temperature increase does not lead apparently to the rate acceleration, which bears upon the faster rates of parallel and consecutive reactions. These are the carbonylative reduction of nitrobenzene (Eq. (*B*)), the reductive carbonylation of nitrobenzene with aniline and CO (Eq. (*C*)) to give DPU, and hydrolysis of DPU (Eq. (*C*)) and DEPU (Eq. (*E*)).

Aniline can be carbonylated also to *N*-phenylformamide (NPF) (Eq. (*F*)) and diethylamine to diethylformamide (Eq. (*G*), even though only to a very small extent.
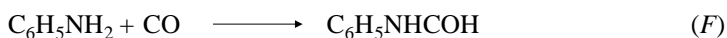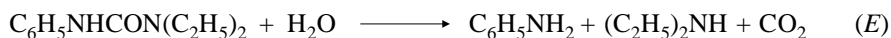
$$C_6H_5NO_2 + H_2O + 3\ CO \xrightarrow{\text{cat.}} C_6H_5NH_2 + 3\ CO_2 \qquad (B)$$

$$C_6H_5NO_2 + C_6H_5NH_2 + 3\ CO \xrightarrow{\text{cat.}} (C_6H_5NH)_2CO + 2\ CO_2 \qquad (C)$$

$$(C_6H_5NH)_2CO + H_2O \longrightarrow 2\ C_6H_5NH_2 + CO_2 \qquad (D)$$

$$C_6H_5NHCON(C_2H_5)_2 + H_2O \longrightarrow C_6H_5NH_2 + (C_2H_5)_2NH + CO_2 \qquad (E)$$

$$C_6H_5NH_2 + CO \longrightarrow C_6H_5NHCOH \qquad (F)$$

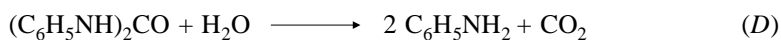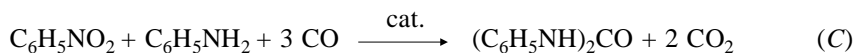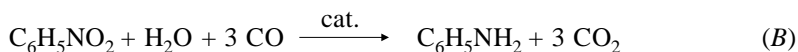$$(C_2H_5)_2NH + CO \longrightarrow (C_2H_5)_2NCOH \qquad (G)$$

TABLE I

The reductive carbonylation of $PhNO_2$ by CO and $Et_2NH$. The influence of temperature on initial reaction rate and selectivity (reactor 500 cm$^3$, 50 g (0.406 mol) $PhNO_2$, $Et_2NH/PhNO_2$ molar ratio = 3 (1.6 wt.% $H_2O$ in $Et_2NH$); 5 g sulfur or 1 g $H_2S$, 0.1 g ammonium metavanadate, initial pressure 13 MPa (298 K))

| Temperature K (±2) | Reaction time h | Initial reaction rate $\Delta P_{30}$, MPa | $X^b$ % | Sectivity$^c$, % | | |
|---|---|---|---|---|---|---|
| | | | | DEPU | $PhNH_2$ | DPU |
| 363 | 5 | 3.1 | 99.5 | 52 | 43 | 5 |
| 383 | 5 | 3.8 | 99.7 | 42 | 47 | 10 |
| 393 | 5 | 6.1 | 99.6 | 54 | 31 | 15 |
| 403 | 4 | 6.0 | 99.3 | 35 | 48 | 12 |
| 413 | 4 | 5.9 | 99.6 | 42 | 47 | 10 |
| 423 | 4 | 4.8 | 99.8 | 48 | 38 | 3 |
| 428 | 4 | 4.2 | 99.5 | 40 | 33 | 19 |
| 443 | 4 | 4.0 | 98.6 | 33 | 50 | 12 |

$^a$ The decrease of pressure after 30 min in MPa. $^b$ Conversion of $PhNO_2$. $^c$ Selectivity calculated to the conversion of $PhNO_2$.

Figure 1 illustrates the effect of the initial CO pressure recalculated to standard conditions, and that both on the reaction rate of the reductive carbonylation (pressure decrease during 30 min, designated as $\Delta P_{30}$), and on the selectivity of DEPU formation. The figure documents the positive effect of the pressure on the selectivity, similarly as the increase of the reaction rate of the carbonylation with increasing pressure.
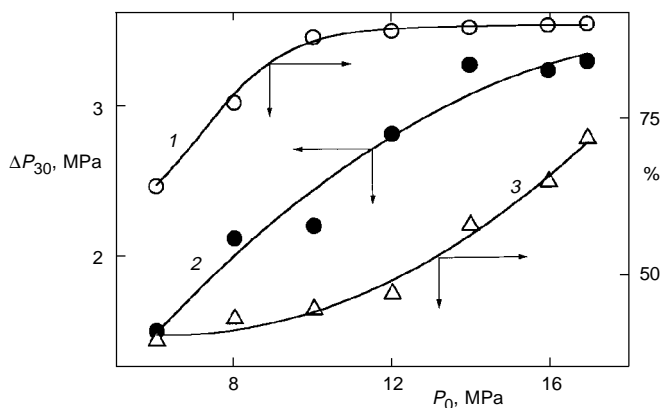


FIG.1

The effect of initial pressure ($P_0$) on reductive carbonylation of nitrobenzene at $403 \pm 2$ K and $Et_2NH/C_6H_5NO_2$ molar ratio = 2 (charge: 50 g $C_6H_5NO_2$, 59.4 g $Et_2NH$, 1 g $H_2S$, and 0.1 g $NH_4VO_3$). *1* $C_6H_5NO_2$ conversion (%), *2* initial rate of reductive carbonylation (expressed by pressure drop during 30 min, $\Delta P_{30}$), *3* selectivity to DEPU (%)
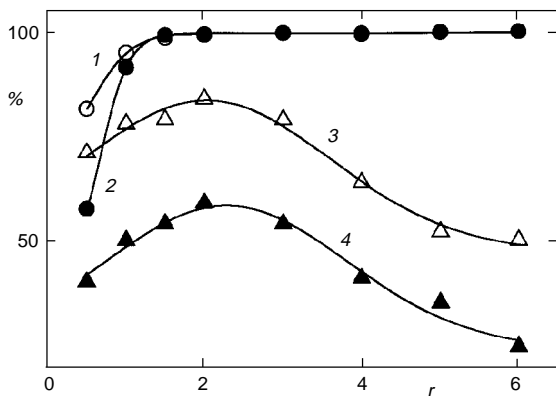


FIG. 2

Effect of $Et_2NH/C_6H_5NO_2$ molar ratio ($r$) on nitrobenzene conversion (%) and DEPU selectivity (%) at $403 \pm 2$ K at CO pressure 13 MPa. Nitrobenzene conversion with $Et_2NH$ containing *1* 1.6 wt.% $H_2O$ and *2* 0.24 wt.% $H_2O$, and DEPU selectivity obtained with $Et_2NH$ containing *3* 1.6 wt.% $H_2O$ and *4* 0.24 wt.% water

Figure 2 shows the effect of the $Et_2NH$ to $C_6H_5NO_2$ molar ratio on the nitrobenzene conversion and on DEPU selectivity for "moist" $Et_2NH$ (containing 1.6 wt.% $H_2O$) and the dry amine (containing 0.24 wt.% $H_2O$; cf. Experimental). Water admixture leads to the greater nitrobenzene conversion also at the $Et_2NH$ to $C_6H_5NO_2$ molar ratio = 0.5, which – besides the reductive carbonylation according to Eq. (*A*) – proceeds also via the carbonylative reduction depicted by Eq. (*B*). The smaller amount of water in the reaction medium increases DEPU selectivity, which manifests itself also in the smaller formation of aniline (Fig. 3). An optimum $Et_2NH$ to $C_6H_5NO_2$ molar ratio seems to be 1 : 2–3. The higher ratio is not necessary, either from the reagent surplus or from the medium basicity which ensures formation of the catalyst proper. The selectivity to DPU is affected negatively by water. Provided that all the components were absolutely dry, the DEPU selectivity would not decrease at the $Et_2NH$ to $C_6H_5NO_2$ molar ratio above 3.

In contrast to the reductive carbonylation of nitrobenzene with CO and methanol to methyl-*N*-phenylcarbamate[7–9], where the addition of base is prerequisite for formation of the catalyst, in our case (Table II), the reactant $Et_2NH$ is also the effective component of the catalytic system. Therefore, the addition of other bases such as triethylamine is not necessary. Furthermore, in the reductive carbonylation with CO and methanol, vanadium(V) species promoted the reaction. The same holds also for the reductive carbonylation under study, although this effect is less pronounced. Both in the absence and presence of ammonium metavanadate, nitrobenzene conversion is nearly complete in 4 h. The promoting effect of the vanadate is documented in Fig. 4. If with $NH_4VO_3$ the pressure drop of about 3.9–4 MPa is observed after 30 min, and nitrobenzene conversion reaches more than 90% after 60 min, then in the absence of this compound, the
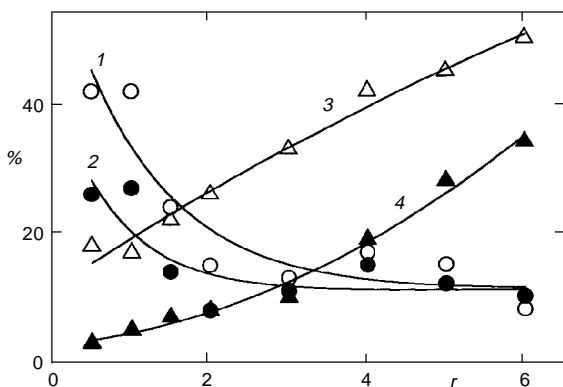


FIG. 3

Effect of molar ratio *r* (cf. Fig. 2) on selectivity to DPU and aniline formation (in %). Selectivity to DPU (*1*) and aniline (*3*) obtained with $Et_2NH$ containing 1.6 wt.% $H_2O$ and analogous data obtained for *2* DPU and *4* aniline with dry $Et_2NH$ (0.24 wt.% $H_2O$)

Effect of components of the catalytic system on the reductive carbonylation of $PhNO_2$ by CO and $Et_2NH$ (reactor 500 $cm^3$, 50 g (0.406 mol) $PhNO_2$, $Et_2NH/PhNO_2$ molar ratio = 3 (1.6 wt.% $H_2O$ in $Et_2NH$); initial pressure 13 MPa (298 K), temperature 403 ± 2 K, reaction time 4 h)

| Run | Catalytic system[a], % | | | Molar ratio $PhNO_2$ : S compound | $X^b$ % | Selectivity[c], % | | | |
|---|---|---|---|---|---|---|---|---|---|
| | S compound | base | $NH_4VO_3$ | | | DEPU | $PhNH_2$ | DPU | NPF |
| 1 | S(10) | – | 0.2 | 1 : 0.4 | 99.5 | 38 | 38 | 18 | 5 |
| 2 | S(10) | – | 0.2 | 1 : 0.4 | 100 | 39 | 37 | 18 | 5 |
| 3 | $CS_2$(10) | – | 0.2 | 1 : 0.32 | 99.6 | 34 | 50 | 10 | 6 |
| 4 | $H_2S$(2) | – | 0.2 | 1 : 0.07 | 99.6 | 31 | 49 | 10 | 10 |
| 5 | $H_2S$(2) | – | 0.2 | 1 : 0.07 | 99.7 | 30 | 48 | 16 | 10 |
| 6 | $H_2S$(2) | – | – | 1 : 0.07 | 94.2 | 30 | 47 | 14 | 11 |
| 7 | $H_2S$(2) | – | – | 1 : 0.07 | 96.2 | 31 | 47 | 12 | 10 |
| 8[d] | $H_2S$(2) | $Et_3N$(6) | 0.2 | 1 : 0.07 | 99.9 | 58 | 23 | 16 | 3 |
| 9 | $CS_2$(2) | $Et_3N$(6) | 0.2 | 1 : 0.07 | 99.9 | 34 | 18 | 11 | 7 |
| 10 | COS(2.5) | – | 0.2 | 1 : 0.05 | 99.9 | 60 | 18 | 20 | 1 |

[a] Wt.% with respect to $PhNO_2$. [b] Conversion of $PhNO_2$. [c] Selectivity calculated to the conversion of $PhNO_2$. [d] The experiment lasted 2.5 h.
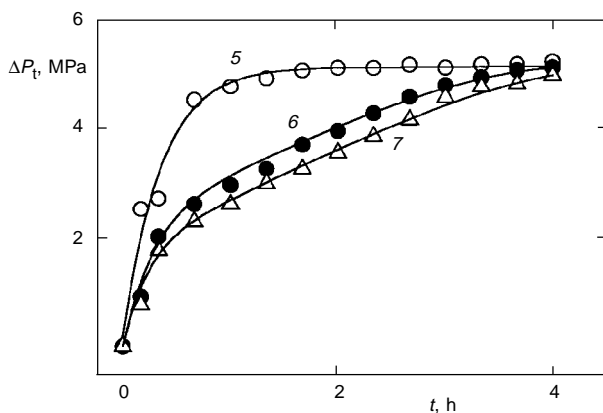


FIG. 4
Comparison of rates of reductive carbonylation of nitrobenzene derived from pressure drop ($\Delta P_t$) in dependence on $NH_4VO_3$ addition (numbering of curves corresponds to designation in Table II). *5* 0.2 wt.% $NH_4VO_3$ (related to the charge of nitrobenzene), *6* and *7* without the vanadate

pressure drop amounts to 2–2.3 MPa after 30 min, and the reaction proceeds at a steady rate for 4 h.

On the other hand, NPF formation increases with increasing amount of water in the reaction system and with decreasing rate of the reductive carbonylation.

Similarly to previous studies[7–9] of the catalytic system used in the present work, also here experiments were carried out to evaluate the effect of its individual components. The most significant effect is exerted by hydrogen sulfide and by carbonyl sulfide, the latter being most likely the CO transfer agent, i.e. the catalyst proper.

As to the sulfur components, their efficiency increases in the following order: $S : CS_2 : H_2S : COS = 1 : 1.2 : 5.7 : 8$.

As found by us in the oxidative carbonylation of aniline with carbon monoxide and oxygen to methyl-*N*-phenylcarbamate[12], with the new catalyst under study, DEPU is formed not only by the reductive carbonylation of nitrobenzene according to Eq. (*A*) but likely also via the oxidative carbonylation of aniline, as described by Eq. (*H*).

$$C_6H_5NH_2 + (C_2H_5)_2NH + 1/2\ O_2 + CO \longrightarrow C_6H_5NHCON(C_2H_5)_2 + H_2O \quad (H)$$

In this connection it is worth mentioning that the analyses of several samples made by gas chromatography yielded the higher content of aniline with respect to data obtained by HPLC, and should be thus corrected. Although this discrepancy was first ascribed by us to a possible decomposition of DEPU at temperatures above 423 K to give phenyl isocyanate and diethylamine (Eq. (*I*)), the direct GLC calibration with phenyl isocyanate showed that the isocyanate is eluted together with aniline.

$$C_6H_5NHCONH(C_2H_5)_2 \longrightarrow C_6H_5NCO + (C_2H_5)_2NH \quad (I)$$
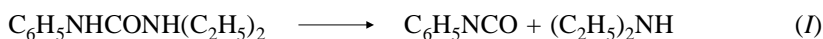
Therefore, we have chosen the more efficient separation system by using the packed column PONA. At temperatures above 423 K we have thus succeeded in determining separately aniline and phenyl isocyanate also from the pure DEPU sample in nonane (cf. Experimental), with proportional amount of diethylamine and nitrobenzene. Thermal decomposition of DEPU under GLC temperatures points to a "non-phosgene" phenyl isocyanate synthesis via DEPU as an intermediate, and analogously also other aryl isocyanates from derivatives thereof.

One can thus expect that the catalytic system under study will catalyze the reductive carbonylation of other mono- and dinitroaromatic hydrocarbons with other alkylamines and dialkylamines to give the corresponding *N*-alkyl-*N*′-arylureas and *N*,*N*-dialkyl-*N*′-arylureas, respectively.

### REFERENCES

1. Patev N., Lachman Z.: Czech. 257 995; Chem. Abstr. *111*, 215539 (1989).
2. Hintermaler H., Michaud H., Obinger M. (SKW Trosberg A.G.): Ger. Offen. 2 742 158; Chem. Abstr. *91*, 20147 (1979).
3. Hearsey C. J., Mehta B. D.: Ger. Offen. 2 258 453 (1973).
4. Hearsey C. J. (Quimico G.m.b.H.): Ger. Offen. 2 317 122; Chem. Abstr. *80*, 14767 (1974).
5. Zajacek J. G., McCoy J. J., Fuger K. E. (Atlantic Richfield Co.): Ger. Offen. 2 453 367 (1975).
6. Tietz H., Schwetlick K., Schobel H. J., Herbid H., Lankau H. J.: GDR 227 700; Chem. Abstr. *104*, 224726 (1986).
7. Macho V., Moravek S., Ilavsky J.: Chem. Papers *43*, 363 (1991).
8. Macho V., Vojcek L., Schmidtova M., Terlandova J.: Collect. Czech. Chem. Commun. *57*, 2605 (1992).
9. Macho V., Vojcek L., Schmidtova M., Harustiak M.: J. Mol. Catal. *88*, 177 (1994).
10. Singliar M., Macho V., Gasparicova E., Stresinkova D.: Chem. Prum. *39*, 254 (1989).
11. Singliar M., Macho V., Terlandova J.: Chem. Papers *43*, 519 (1989).
12. Macho V., Harustiak M.: J. Mol. Catal. *91*, L 155 (1994).