Catalytic reductive carbonylation of nitrobenzene to methyl N-phenylcarbamate

[a]V MACHO, [b]Š. MORÁVEK, and [a]J. ILAVSKÝ

[a]Department of Organic Technology, Faculty of Chemical Technology,
Slovak Technical University, CS-812 37 Bratislava

[b]Department of Chemistry and Technology of Petroleum, Faculty of Chemical Technology,
Slovak Technical University, CS-812 37 Bratislava

A new three-component catalytic system (S and its compounds + + CH_3COONa + V_2O_5) can be used for reductive carbonylation of $PhNO_2$ with CO and CH_3OH which gives methyl N-phenylcarbamate and aniline. The initial carbon monooxide pressure is equal to 14 MPa at 298 K and the reaction takes place at 360—470 K. Moreover, the influence of components (S or CS_2 and V_2O_5) of the catalytic system as well as of water addition on initial reaction rate and selectivity of the reaction has been examined. The reaction mechanism is discussed. It has been proved that the hydrogen from water molecule is taking part only indirectly in the reaction with $PhNO_2$ to give $PhNH_2$.

The reductive carbonylation of aromatic nitro compounds with carbon monooxide in the presence of alcohols, which yields alkyl N-arylcarbamates, can be catalyzed by the system consisting of compounds of rare metals of the VIIIth group of the periodic system (Pd, Pt, Rh, Ru) and the Lewis acids [1—4]. Beside this a multicomponent system on the basis of selenium, sulfur and their compounds and further three or four components [5—8] can be used. In these cases however, there are problems concerning the reproducibility.

We have found a new three-component catalytic system on the basis of sulfur and its compounds (CS_2, COS, H_2S, and others), alkaline salt of a weak carboxylic acid (CH_3COONa) and vanadium(V) oxide. Moreover, the activation effect of the controlled amount of oxygen appeared to be significant [9]. We investigated the influence of temperature, components of the catalytic system and water on initial reaction rate as well as on selectivity of the methyl N-phenylcarbamate and aniline formation in the case of reductive carbonylation of nitrobenzene in the presence of methanol.

Experimental

Chemicals used: nitrobenzene, chemically pure, containing 0.4 mass % of water (Lachema, Brno); methanol, anal. grade, containing 0.25 mass % of water (Lachema,

Brno); methanolic solution of sodium methoxide (10 mass %) prepared from anhydrous methanol and sodium; carbon monooxide containing 1.8 vol. % of hydrogen, 0.2 vol. % of oxygen, 0.8 vol. % of nitrogen, and 0.1 vol. % of carbon dioxide; elemental sulfur, chemically pure, sublimated powder; vanadium(V) oxide, chemically pure; sodium acetate, anhydrous, anal. grade.

Carbonylation procedure

We investigated the influence of temperature (in the range 360—470 K) using a constant content of reaction components (100 g $PhNO_2$ and 200 g MeOH) and the same catalytic system (10 g S, 10 g CH_3COONa, and 1.2 g V_2O_5) in a rotating autoclave from stainless steel (volume of 1 dm^3). The initial pressure of carbon monooxide was 12—16.5 MPa at 25 °C in order the total pressure in the autoclave could reach 21—22 MPa after the expected reaction temperature had been attained. Furthermore, the content of oxygen in the reaction medium was raised by blowing pure oxygen at the pressure of 0.1 MPa and thus removing air from the autoclave. Without the addition of oxygen the reductive carbonylation was less reproducible. The total time of experiment after attaining the necessary temperature was equal to 3 h. The temperature and pressure were recorded in the intervals of 3—5 min.

Using a similar composition of the batch in autoclave and initial pressure of carbon monooxide equal to 14 MPa at 25 °C the quantity of sulfur present either in elemental or in CS_2 form was varied at (150 ± 1) °C. The influence of the amount of V_2O_5 was also investigated at a constant amount of elemental sulfur (10 g). A similar batch as used for investigation of the influence of temperature and equal conditions (temperature (150 ± 1) °C, initial pressure of CO 14 MPa at 25 °C) were applied for the study of the influence of water additions.

The reaction rate of the reductive carbonylation of $PhNO_2$ was calculated from the decrease of overall pressure in the autoclave related to standard conditions. The rate constant was obtained from the integrated form of the kinetic equation for reaction of the first order

$$k = \frac{1}{t} \ln \frac{p_0 - p_k}{p_t - p_k}$$

where k/min^{-1}, p_0, p_k, and p_t (MPa) are the rate constant, pressure at the beginning, at the end of reaction, and in the time t, respectively.

The composition of the liquid product (containing only insignificant amount of components of the catalytic system) was determined by the liquid—gas chromatography [10—12].

Results and discussion

By plotting $\ln \dfrac{p_0 - p_k}{p_t - p_k}$ against time in the temperature range 360—470 K we obtained linear dependences, which means that the reaction follows the kinetics of the first-order reactions in the above temperature interval. This fact is

confirmed also by the dependence of $\ln k$ as a function of reciprocal temperature presented in Fig. 1. For the dependence of the rate constant k on temperature $\langle 360-470\ \mathrm{K} \rangle$ it can be written

$$\ln (k/\mathrm{min}^{-1}) = 1.7394 \pm 0.4783 - \frac{2580.80 \pm 196.57}{T}$$

the apparent activation energy being $E = (21.5 \pm 1.6)\ \mathrm{kJ\ mol}^{-1}$
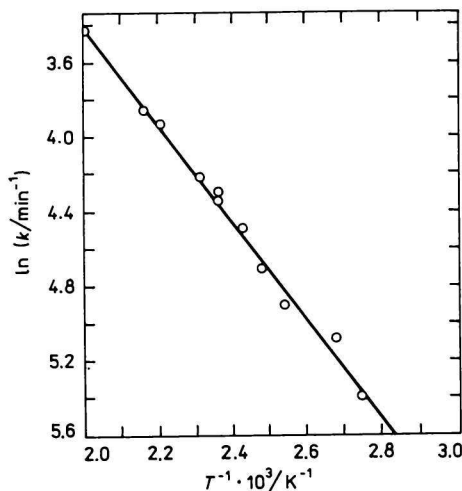

Fig. 1. Dependence of the rate constant k of reductive carbonylation of nitrobenzene on reciprocal value of absolute reaction temperature at constant amount and composition of the catalytic system and constant pressure (20—22 MPa).

The results of the study of the influence of temperature in isochronal experiments on overall conversion of $PhNO_2$ as well as on selectivity referred to methyl N-phenylcarbamate and aniline are given in Table 1. On the other hand, the

Table 1

Influence of temperature on reductive carbonylation of nitrobenzene at constant initial pressure of CO for invariable amount and composition of the catalytic system in isochronal experiments

T/K	Conversion of $PhNO_2$	$k \quad 10^2$	Selectivity/%	
	%	min^{-1}	Methyl N-phenylcarbamate	Aniline
363.15	8.4	0.457	43.1	56.9
373.15	15.9	0.617	67.3	32.7
393.15	52.1	0.750	94.4	3.1
403.15	98.9	0.901	91.8	8.2
413.15	100.0	1.122	90.3	9.4`
423.15	97.0	1.334	94.5	4.7
423.15	99.7	1.350	88.9	10.1
433.15	98.1	1.477	91.1	8.9
453.15	99.7	1.926	85.0	15.0
463.15	95.3	2.112	81.3	19.7

Influence of the amount of sulfur or carbon disulfide on the reaction and selectivity of reductive carbonylation of nitrobenzene at initial CO pressure of 14 MPa (25°C) and at the temperature $(150 \pm 1)°C$

Sulfur		Conversion of PhNO$_2$	$k \cdot 10^2$	Selectivity/%	
Form	$\dfrac{m(S)}{m(PhNO_2)} \Big/ \%$	%	$\overline{mi^{-1}}$	Methyl N-phenylcarbamate	Aniline
S	1	4.0	0.19	0.0	100
S	5	32.4	0.35	61.5	26.9
S	7	54.8	0.45	86.8	13.8
S	10	·99.9	0.69	90.0	9.9
S	15	100.0	1.18	87.4	11.5
CS$_2$	1	6.8	0.30	0	100
CS$_2$	1.5	11.3	0.51	32.6	64.6
CS$_2$	2.0	21.6	0.73	46.8	53.7
CS$_2$	3.0	28.5	1.12	63.2	36.8
CS$_2$	5.0	99.0	1.38	86.7	11.9
CS$_2$	7.0	99.9	1.59	91.4	8.1
CS$_2$	10.0	99.9	2.62	85.9	13.4

influence of the quantity of elemental sulfur or carbon disulfide as component of the catalytic system on reaction rate and selectivity of the reductive carbonylation of PhNO$_2$ is presented in Table 2. The influence of the quantity of vanadium(V) oxide as another component of the catalytic system on conversion of PhNO$_2$ achieved in isochronal experiments (lasting 3 h) at $(150 \pm 1)°C$ is presented in Fig. 2. The obtained results show that sulfur is more efficient if it
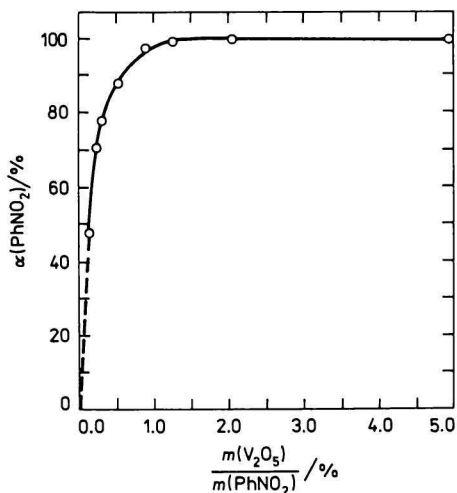

Fig. 2. Influence of vanadium(V) oxide on conversion of nitrobenzene in isochronal experiments.

is present in the form of carbon disulfide. It seems that all three components of this catalytic system are precursors of an efficient catalyst of reductive carbonylation. It is therefore not surprising that the rate of reductive carbonylation as well as the selectivity referred to methyl N-phenylcarbamate is low not only at low reaction temperature ($T < 373$ K) but also at a low content of some components in the catalytic system. However, a high selectivity of aniline formation can be achieved by the addition of water to starting raw materials (CH_3OH and $PhNO_2$). This assumption is also confirmed by the results obtained by investigation of the influence of water added into the reaction medium on selectivity of methyl N-phenylcarbamate and aniline formation in the course of complete conversion of nitrobenzene (Fig. 3).
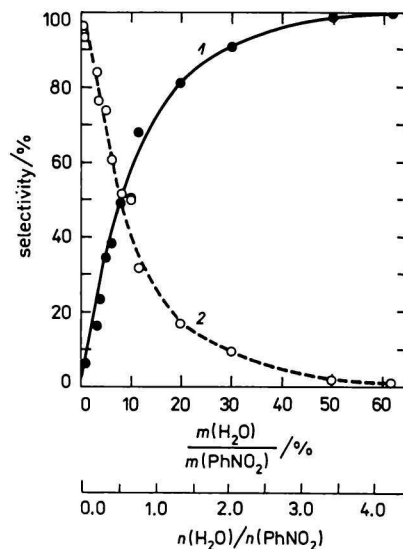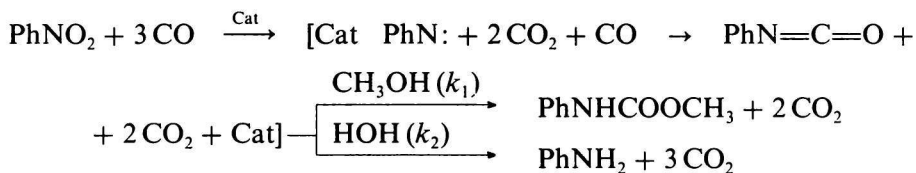

Fig. 3. Influence of water on selectivity of methyl N-phenylcarbamate and aniline formation for complete (100%) conversion of nitrobenzene produced by carbonylation. 1. Selectivity of aniline formation; 2. selectivity of methyl N-phenylcarbamate formation.

In the reaction medium at the mole ratio MeOH/$PhNO_2$ 6.44 the selectivity with respect to methyl N-phenylcarbamate is over 95% when no water has been added. However, if 25 mass % of water (referred to $PhNO_2$) have been added, *i.e.* the mole ratio H_2O/$PhNO_2$ has been adapted to 1.7, the selectivity of methyl N-phenylcarbamate formation is only 13% and of aniline 87%. For the mole ratio H_2O/$PhNO_2$ equal to 3 the selectivity of aniline formation already reaches 97.5%. In accordance with expectation, aniline is formed from nitrobenzene and water also in the medium of acetone at 150°C and at the pressure of carbon monooxide 10—22 MPa in complete conversion with utter selectivity.

It appears that both methyl N-phenylcarbamate and aniline arise from the common precursor or intermediate (nitrene, phenyl isocyanate or other inter-

mediary product) from which methyl(alkyl) *N*-phenylcarbamate is formed in the presence of methanol (alcohol) (reaction characterized by the rate constant k_1) while aniline is formed in a competition reaction characterized by the rate constant k_2. This competition reaction is much faster in the presence of reactive water which is more acid, polar, hydrophilic and less bulky than methanol; thus it holds $k_1 \ll k_2$.

$$PhNO_2 + 3\,CO \xrightarrow{\text{Cat}} [Cat \quad PhN: + 2\,CO_2 + CO \rightarrow PhN{=}C{=}O +$$

$$+ 2\,CO_2 + Cat] - \boxed{\begin{array}{c} CH_3OH\,(k_1) \\ \hline HOH\,(k_2) \end{array}} \begin{array}{l} \longrightarrow PhNHCOOCH_3 + 2\,CO_2 \\ \longrightarrow PhNH_2 + 3\,CO_2 \end{array}$$

We can assume that the first elementary step of the reaction mechanism involves the formation of COS from S and CO and in the presence of CH_3COONa a complex with $PhNO_2$ is formed. Thus the NO_2 groups are reduced to give a nitrene group —N: and carbon dioxide. The nitrene group is liable to react with CO and the intermediary phenyl isocyanate quickly reacts either with H_2O to give $PhNH_2$ or with CH_3OH to give $PhNHCOOCH_3$. This idea is supported by the favourable effect of oxygen addition to the reaction system observed by us [9] as well as by the positive effect of vanadium(V) oxide.

Thus the hydrogen from water takes part only indirectly in the reduction of nitrobenzene to aniline.

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