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Palladium Catalysed Conversion of *N*,*N*′-Diphenylurea into Carbamate Esters

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Abstract

$PdCl_2(PhNH_2)_2$ catalyses the conversion of *N*,*N*′-diphenylurea into alkyl *N*-phenylcarbamate under CO and O_2 pressures at temperatures higher than 100 °C. The reaction rate and yields grow with increasing CO and O_2 pressures and in the presence of $CuCl_2(PhNH_2)_2$. The conversion is accomplished through the following reactions:

$$CO(NHPh)_2 + ROH \rightleftharpoons PhNHCOOR + PhNH_2$$

$$2PhNH_2 + CO + \tfrac{1}{2}O_2 \longrightarrow CO(NHPh)_2 + H_2O$$

Due to a side reaction, some amounts of carbon dioxide are also obtained.

Introduction

Carbamate esters are valuable compounds, widely used either in agriculture, as chemicals and pesticides, or in industry, as intermediates for preparing isocyanates, urethanes and polyurethanes. Carbamates are usually obtained from the reaction of alcohols with isocyanate, whose preparation involves the use of the dangerous chemical phosgene. In the last decade, new methods of synthesis (reactions (1) and (2)), based on the catalytic activity of transition metal complexes, have been described [1] and many catalyst systems have been patented for these reactions.

$$ArNO_2 + 3CO + ROH \longrightarrow ArNHCOOR + 2CO_2 \quad (1)$$

$$ArNH_2 + CO + \tfrac{1}{2}O_2 + ROH \longrightarrow ArNHCOOR + H_2O \quad (2)$$

Carbamates have also been obtained from both the conversion of diethylcarbonate [2] and *N*,*N*′-disubstituted ureas [3], and from the reaction of CO_2 with amines [4]. Recently we have found [5] that, under mild conditions (70–90 °C and an atmospheric pressure of CO/O_2 mixture) some $PdCl_2L_2$ complexes ($L = CH_3CN$, p-$RC_6H_4NH_2$; $R = H, Cl, CH_3$) promote the oxidative carbonylation of alkyl and aryl primary amines, giving *N*,*N*′-disubstituted ureas. Under more drastic temperature and pressure conditions the same systems produce both ureas and carbamates. Our idea was that, carbamates are not formed by direct interaction of aniline, CO and alcohol, but through the alcoholysis of the urea. If this is correct, it is to be expected that the $PdCl_2L_2$ systems would convert catalytically *N*,*N*′-disubstituted ureas into carbamate esters. The reaction involved would be, in such a case, alcoholysis of urea followed by oxidative carbonylation of the amine produced. We report the results of this research below.

Results

When *N*,*N*′-diphenylurea was heated in a methanol solution under a nitrogen atmosphere at temperatures higher than 100 °C, aniline and methyl-*N*-phenylcarbamate were produced in a 1:1 ratio, according to the equilibrium of the alcoholysis reaction (3).

$$CO(NHPh)_2 + MeOH \rightleftharpoons CO(NHPh)(OMe) + PhNH_2 \quad (3)$$

By carrying out the reaction under pressures of a 2/1 CO/O_2 mixture, where catalytic amounts of $PdCl_2(PhNH_2)_2$ were present, an increase in the carbamate was observed with a simultaneous decrease in aniline. These results can be explained by assuming that the *N*,*N*′-diphenylurea is converted into methyl-*N*-phenylcarbamate according to reaction (4).

$$CO(NHPh)_2 + 2MeOH + \tfrac{1}{2}O_2 + CO \longrightarrow 2CO(NHPh)(OMe) + H_2O \quad (4)$$

We believe that reaction (4) is the outcome of two independent reactions: the first one, the alcoholysis of urea (reaction (3)); the second one, the oxidative carbonylation of aniline (reaction (5)).

$$2PhNH_2 + CO + \tfrac{1}{2}O_2 \longrightarrow (PhNH)_2CO + H_2O \quad (5)$$

In this view, reaction (5) is the truly catalysed reaction which we have shown to occur [5] through reactions (6) and (7).

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TABLE I. N,N'-Diphenylurea Conversion Using $PdCl_2(PhNH_2)_2$ (A) and $CuCl_2(PhNH_2)_2$ (B)[a]

Catalyst	Reagent[b]	Solvent	Temperature (°C)	Time (h)	Pressure CO/O_2 (atm)	Carbamate mmol (%)
none	N,N'-urea	methanol	150	3	none[c]	1.65[d]
A	N,N'-urea	methanol	150	10	30	3.35(71)
A	N,N'-urea	methanol	150	3	30	2.76(58)
A + B	N,N'-urea	methanol	150	3	30	3.40(72)
A + B	N,N'-urea	methanol	150	6	30	4.20(89)
A	N,N'-urea	ethanol	150	6	30	3.31(70)
A + B	N,N'-urea	ethanol	150	6	30	4.29(91)
A + B	N,N'-urea	butanol	150	6	30	3.07(70)
A + B	N,N'-urea	methanol	130	3	30	2.54(54)
A + B	N,N'-urea	methanol	120	3	30	2.51(53)
A + B	N,N'-urea	methanol	150	3	20	3.12(66)
A + B	N',N'-urea	methanol	150	3	10	2.58(55)
A + B	N,N'-urea	methanol	150	3	1	1.71(36)
A + B	N,N'-urea + $C_6H_5NH_2$ (0.4)	methanol	150	6	30	5.22(> 100)
A + B	$C_6H_5NH_2$ (22.0)	methanol	150	6	30	3.18[e]
A + B	$C_6H_5NH_2$ (22.0)	ethanol	150	6	30	3.21[f]
A + B	$C_6H_5NH_2$ (22.0)	methanol	130	10	1	trace

[a] In all reactions the used amounts were: $PdCl_2(PhNH_2)_2$ (0.28 mmol), $CuCl_2(PhNH_2)_2$ (0.40 mmol), N,N'-diphenylurea (2.36 mmol), alcohol (10 ml). [b] mmol in parentheses. [c] Under nitrogen atmosphere. [d] Aniline (1.48 mmol) was also obtained. [e] N,N'-Diphenylurea (1.95 mmol) was also obtained. [f] N,N'-Diphenylurea (1.88 mmol) was also obtained.

$$PdCl_2(PhNH_2)_2 + 2PhNH_2 + CO \longrightarrow CO(NHPh)_2 + 2PhNH_3^+Cl^- + Pd \quad (6)$$

$$Pd + 2PhNH_3^+Cl^- + \tfrac{1}{2}O_2 \longrightarrow PdCl_2(PhNH_2)_2 + H_2O \quad (7)$$

The following experimental results support the above assumption: (i) Both alkyl-N-phenylcarbamate and N,N'-diphenylurea were yielded when aniline was allowed to react with CO/O_2 in methanol or ethanol at temperatures higher than 100 °C and above atmospheric pressure. (ii) By carrying out the urea conversion in the presence of aniline, the carbamate amounts were higher than that expected from reaction (5) stoichiometry.

The results of the more significative experiments have been summarized in Table I. Three different alkyl-carbamates $C_6H_5NHCOOR$ (R = Me, Et, n-But) were obtained by carrying out the reaction in the respective solvents. A growth in yields was observed with increasing CO and O_2 pressures while a scarce influence of temperature in the range 130–150 °C was observed; also the addition of catalytic amounts of $CuCl_2(PhNH_2)_2$ was benficial to the reaction and, therefore, the best results were obtained with the $PdCl_2/CuCl_2$–aniline system. However, independently of the temperature, a low conversion was obtained when the catalysis was carried out under the atmospheric pressure of the CO/O_2 mixture. In fact, under these conditions, the carbamate amounts were nearly the same as those produced when the reaction was achieved under nitrogen. This last result and the above mentioned temperature and pressure influence suggest that the carbon monoxide coordination to palladium (reaction (8)), could be a key step in the catalysis.

$$PdCl_2(PhNH_2)_2 + CO \rightleftarrows PdCl_2(PhNH_2)_2CO \quad (8)$$

Under alcoholysis temperature conditions ($T >$ 100 °C), the concentration of the carbonyl complex $PdCl_2(PhNH_2)_2CO$, would be very low and, therefore, a higher carbon monoxide pressure would be required to shift the equilibrium (8) to the right in order to accomplish the catalysis. Further support for this statement comes from experimental results which showed that the aniline carbonylation according to reaction (4) was not accomplished under the atmospheric pressure of a CO/O_2 mixture at temperatures ranging from 110–130 °C.

In all the experiments some amounts of CO_2 were observed. The CO_2 formation has already been observed with Pd(II)–Cu(II) systems [6] and it can be derived either from a nucleophilic attack of a water molecule on the CO coordinated to the palladium, or from hydrolysis of the carbamate and successive decomposition in CO_2 and aniline of the resulting carbamate acid. However, control experiments showed that by heating methylcarbamate in an ethanol–water (95:5) solution under the urea conversion conditions trace amounts of CO_2 were detected.

Experimental

A Carlo Erba Fractovap C gas chromatograph with a thermal conductivity detector connected to a Hewlett Packard 3380A integrator was used and separation of gas mixtures was achieved on a Porapak Q column. GLC analyses were carried out with a GP 20% SP 2100 0.1% carbowax 1.8 column on a Varian Vista 6000 gas chromatograph connected to a Varian Vista 4270 integrator. Toluene was used as an internal standard.

N,N'-Diphenylurea Conversion into Methyl-N-phenylcarbamate Under CO and O_2 Pressures

$PdCl_2(PhNH_2)_2$ (0.28 mmol), $CuCl_2(PhNH_2)_2$ (0.40 mmol), *N,N'*-diphenylurea (2.36 mmol) and methanol (10 ml) were placed in a stainless steel autoclave (55.6 ml) which was charged with O_2 (10 atm) and then with CO to a total pressure of 30 atm. The autoclave was mounted in an electrical oven and allowed to react to the prefixed temperature. After 6 h, the autoclave was cooled and its contents (gas and solution) were gas-chromatographically analysed. Methyl-*N*-phenylcarbamate (4.20 mmol) 89% of the expected amount on the basis of stoichiometry of reaction (4) and a trace amount of $PhNH_2$ were detected in solution; some CO_2 was also observed in the gas phase.

The reactions under different conditions of CO and O_2 pressures and temperatures were carried out as above and the yields are reported in Table I.

Ethyl-N-phenylcarbamate and n-Butyl-N-phenylcarbamate

The reactions were carried out in the respective solvents (ethanol and n-butanol) according to the above procedure. The yields are reported in Table I.

N,N'-Diphenylurea Conversion in the Presence of Aniline

$PdCl_2(PhNH_2)_2$ (0.28 mmol), $CuCl_2(PhNH_2)_2$ (0.40 mmol), *N,N'*-diphenylurea (2.36 mmol), aniline (5.5 mmol) and methanol (10 ml) were charged into the autoclave which was pressurized with O_2 (10 atm) and CO to a total pressure of 30 atm. Then the temperature was raised to 150 °C for 6 h. After cooling, the reaction solution contained methyl-*N*-phenylcarbamate (5.22 mmol), $PhNH_2$ (2.80 mmol) and *N*-methylaniline (0.75 mmol) and one unidentified product.

Aniline Conversion into Methyl-N-phenylcarbamate

$PdCl_2(PhNH_2)_2$ (0.28 mmol), $CuCl_2(PhNH_2)_2$ (0.40 mmol), $PhNH_2$ (22.0 mmol) and methanol were made to react in the autoclave under a CO and O_2 mixture to a total pressure of 30 atm. After 6 h, the autoclave was cooled, the contents filtered and a residue of *N,N'*-diphenylurea (1.95 mmol) was separated. The filtered solution was analysed by gas chromatography and methyl-*N*-phenylcarbamate (3.18 mmol), *N*-methylaniline and aniline were detected.

The reaction in ethanol was carried out as above and the results are reported in Table I.

N,N'-Diphenylurea Alcoholysis

N,N'-diphenylurea (2.36 mmol) and methanol (10 ml) were placed in the autoclave under a nitrogen atmosphere and allowed to react at 150 °C. After 3 h the autoclave was cooled and its contents were analysed. Aniline (1.58 mmol) and methyl-*N*-phenylcarbamate (1.65 mmol) were the only observed products. The same results were obtained when the reaction was carried out under an atmospheric pressure of a 2/1 CO/O_2 mixture.

Reaction of Aniline With CO and O_2 at 120 °C Under Atmospheric Pressure

$PdCl_2(PhNH_2)_2$ (0.28 mmol), aniline (22.0 mmol) and methanol (10 ml) were placed in a glass reactor (130 ml) and allowed to react at 120 °C under the atmospheric pressure of a 2/1 CO/O_2 mixture. After 12 h the reaction mixture was filtered and palladium metallic (0.020 g) was separated. The resulting filtered solution was evaporated *in vacuo* and trace amounts of *N,N'*-diphenylurea were obtained.

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