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Synthesis of dialkylureas by electrocatalytical carbonylation of aliphatic amines under mild conditions

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Abstract

A novel synthesis of several dialkylureas by electrocatalytical carbonylation of aliphatic amines was investigated at 30°C and atmospheric pressure in the presence of Pd(II) and Cu(II) cocatalyst. This catalyst system was very effective for the carbonylation of primary mono-amines. Furthermore, the phenomenon of the non-Faradic electrochemical modification of catalytic activity was observed in this homogeneous reaction system and the current efficiency for dialkylurea formation reached 401%. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbon monoxide; Electrocatalysis; Aliphatic amines; Carbonylation; Dialkylurea

1. Introduction

Disubstituted ureas have been found to be very useful as precursors for pesticides, pharmaceuticals, and resins [1,2]. In the past two decades, several methods for synthesis of the urea derivatives have been developed [3], and the catalytic oxidative carbonylation of amines with carbon monoxide in the presence of various catalysts, such as Ni [4], Co [5], Mn [6], Rh [7], Ru [8], Se [9], W [10,11] and the most commonly Pd [12–14] has been extensively studied. Generally, the drastic reaction conditions, e.g. high pressure and dangerous CO/O_2 gas mixture have been inevitably employed. The use of oxygen also implies the formation of water and causes undesired side reactions.

The oxidative carbonylation reactions could be performed by a suitable electrocatalytical oxidative carbonylation at atmospheric pressure and relatively low reaction temperature in which there is no oxygen involved. So, no water is formed, side reactions can be also inhibited and the performances of the catalysts should be enhanced. In the present work, we report such a process for the synthesis of dialkylureas by electrocatalytical carbonylation of a series of aliphatic amines through a $Pd(PPh_3)_2Cl_2 + Cu(OAc)_2$ catalyst system under mild reaction conditions:

$$2RNH_2 + CO \xrightarrow[\substack{Bu_4NClO_4, 30^\circ C, 1\,atm \\ 0.9\,V\ versus\ SCE}]{Pd(PPh_3)_2Cl_2 + Cu(OAc)_2} RNHCONHR \quad (1)$$

2. Experimental

2.1. Materials and apparatus

CH_3CN and CH_3OH were purified by distillation prior to use. $Pd(PPh_3)_2Cl_2$ complex was formed in situ by addition of $PdCl_2$ (0.08 mmol) and the ligand

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(0.16 mmol) to the electrolytic solution presaturated with carbon monoxide (99.99%). All other reagents were used without further purification. A CHI660A (CH Instruments, USA) electrochemical workstation was used to control the reaction system and to record the current and the amount of passed electricity in all experiments. A conventional divided H-type cell reactor was used in which the anodic zone was equipped with a gas inlet and outlet, a magnetic stirrer, reference (SCE), and working electrodes (compact graphite, 5 cm^2 apparent surface). Before using, the working electrode was polished with 0.3 μm alumina/water slurry and cleaned supersonically in distilled water. The reaction temperature was controlled by a thermostatic bath.

2.2. Cyclic voltammetry

Cyclic voltammetry was carried out in 70 ml CH_3CN solvent + 0.007 mol Bu_4NClO_4 as supporting electrolyte. The graphite electrode (1.0 cm × 0.5 cm × 0.2 cm) was employed as working electrode and counter electrode. The anode potentials were referred to SCE. Cyclic potential sweeps were generated by the CHI660A electrochemical workstation. The scan rate was 50 mV/s from −0.4 to 1.2 V, and the electrochemical measurements were carried out at 30°C.

2.3. Procedures of electrocatalytic carbonylation reaction and analyses

Experiments were performed at constant anodic potential (0.9 V versus SCE). For each reaction, 0.007 mol Bu_4NClO_4 as supporting electrolyte + 70 ml solvent was charged into the reactor at 30°C, and then the reactor system was purged with carbon monoxide (99.99%) at the rate of 1 bubble/s for ca. 0.5 h in order to remove air. Pd complex (0.08 mmol) and/or $Cu(OAc)_2$ (0.1 mmol) as catalysts and substrate amine (10 mmol) were added successively into the reactor, and then the desired potentials were switched on. The reaction was typically allowed to proceed for 10 h. After the reaction, the product analysis was performed with an HP6890/5793 GC–MS equipped with an HP-5MS column (cross-linked with 5% PH Me siloxane, 30 m). The concentration of reactant and product was directly given by the system of GC–MS chemstation according to the area of each chromatograph peak.

3. Results and discussion

3.1. Cyclic voltammetry of amine and catalysts

The cyclic voltammograms of *n*-butylamine, $Pd(PPh_3)_2Cl_2 + Cu(OAc)_2$ catalysts and *n*-butylamine under reaction conditions in CH_3CN are shown in Figs. 1–4, respectively. No electrocatalytical wave was observed in the case of *n*-butylamine between −0.4 and 1.2 V, when there was no catalyst in the solution (Fig. 1). This is consistent with the fact that aliphatic amines have higher oxidative potential in CH_3CN [15]. Tsuji and Minato [16], Backvall and Gogoll [17], and Horowitz [18] have shown that metallic Pd(0) can be regenerated into Pd(II) in electrochemical system during the Wacker oxidation of olefins, and a homogeneous electron transfer agent such as benzoquinone or $FeCl_3$ was used in order to keep the reduced Pd(II) to be reoxidized during the reaction. In this work, $Cu(OAc)_2$ was chosen for the electron transfer agent at the beginning. No electrocatalytical wave was observed for $Pd(PPh_3)_2Cl_2$ between −0.4 and 1.2 V, while the cyclic voltammogram of $Pd(PPh_3)_2Cl_2 + Cu(OAc)_2$ catalysts shown in Fig. 2 was similar to that of $Cu(OAc)_2$ (not shown).

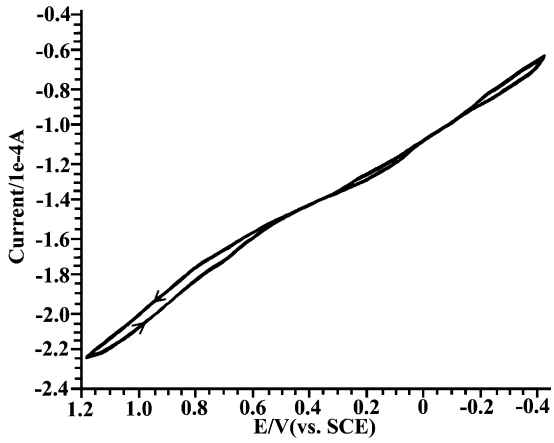

Fig. 1. The cyclic voltammograms of *n*-butylamine in acetonitrile. The solution consisting of 0.03 mol/l *n*-butylamine, 0.1 mol/l Bu_4NClO_4 at 30°C; graphite working electrode; scan rate 50 mV/s.

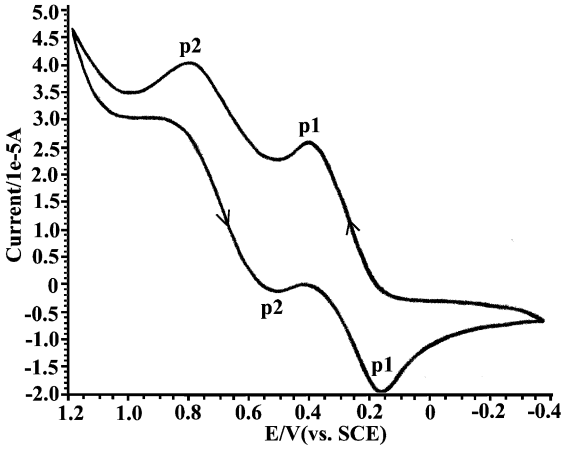

Fig. 2. The cyclic voltammograms of 0.003 mol/l $Cu(OAc)_2$ and 0.0015 mol/l $Pd(PPh_3)_2Cl_2$. The solution consisting of 0.1 mol/l Bu_4NClO_4 at 30°C; graphite working electrode; scan rate 50 mV/s; the CV obtained after the first cyclic sweep.

Therefore, the two pairs of redox couples (p1 and p2) in the region of sweep potential were attributed to the redox transition of Cu(0)/Cu(I) and Cu(I)/Cu(II), respectively, i.e. Cu(I) was electrocatalytically reoxidized to Cu(II) at above 0.5 V. Because the cyclic voltammetries of *n*-butylamine under reaction conditions were done under CO bubbling and with stirring,

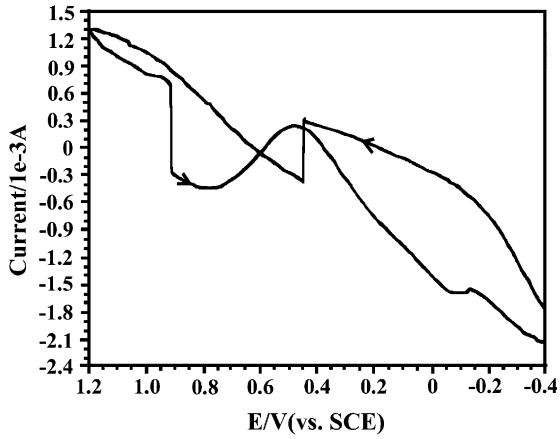

Fig. 3. The cyclic voltammograms of *n*-butylamine under reaction conditions. The solution consisting of 0.03 mol/l *n*-butylamine, 0.1 mol/l Bu_4NClO_4, 0.003 mol/l $Cu(OAc)_2$, 0.0015 mol/l $Pd(PPh_3)_2Cl_2$, and 0.1 mol/l Bu_4NClO_4 at 30°C; CO was bubbled through at a rate of 1 bubble/s; graphite working electrode; scan rate 50 mV/s.

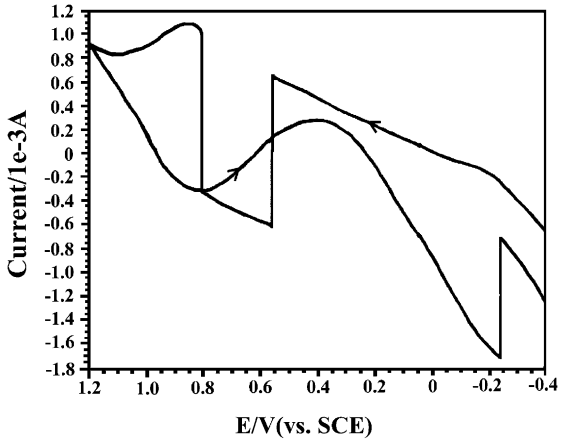

Fig. 4. The cyclic voltammograms of *n*-butylamine under reaction conditions after the first cyclic sweep. The solution consisting of 0.03 mol/l *n*-butylamine, 0.1 mol/l Bu_4NClO_4, 0.003 mol/l $Cu(OAc)_2$, 0.0015 mol/l $Pd(PPh_3)_2Cl_2$, and 0.1 mol/l Bu_4NClO_4 at 30°C; CO was bubbled through at a rate of 1 bubble/s; graphite working electrode; scan rate 50 mV/s.

there was interference during the experiments and it made the curves bounce. During the first cyclic potential sweep, the oxidative peak of the Cu(I)/Cu(II) transition at 0.8 V disappeared and there was only one wave observed at about 0.4 V during the reductive sweep, which was attributed to the oxidative transition of Cu(0) to Cu(I) (Fig. 3). While during the second cyclic sweep, both oxidative peaks of Cu(0)/Cu(I) and Cu(I)/Cu(II) appeared (Fig. 4). This is taken to indicate the existence of redox transition of Cu(0)/Cu(II) during the reaction, and the results proved that $Cu(OAc)_2$ does take part in the reaction process. In order to achieve reasonably rapid reoxidation of Cu(I) and at same time to avoid the direct decomposition of amine, the electrocatalytical carbonylation was performed at 0.9 V versus SCE.

3.2. Electrocatalytical carbonylation of aliphatic amines

The experimental results on the electrocatalytical carbonylation of a series of aliphatic amines with different catalysts and solvents indicated that the carbonylation reactions occurred under mild reaction conditions, as shown in Table 1. For the aliphatic mono-amines (entries 1–10), the GC–MS analysis

Table 1
Results of electrocatalytical carbonylation of aliphatic amines

Entry	Substrate amine	Solvent	Catalyst	Charge (C)	CE vs. dialkylurea (%)[a]	Conversion (%)	Selectivity	
							Dialkylurea (%)	Isocyanate (%)
1	n-$BuNH_2$	CH_3CN	$Cu(OAc)_2$	269	158	51	76	24
2	n-$BuNH_2$	CH_3CN	$PdCl_2$	239	299	78	92	8
3	n-$BuNH_2$	CH_3CN	$Pd(OAc)_2 + Cu(OAc)_2$	272	326	93	97	3
4	n-$BuNH_2$	CH_3CN	$Pd(PPh_3)_2Cl_2 + Cu(OAc)_2$	250	378	100	98	2
5	t-$BuNH_2$	CH_3CN	$Pd(PPh_3)_2Cl_2 + Cu(OAc)_2$	248	335	88	96	4
6	$CH_3(CH_2)_4CH_2NH_2$	CH_3CN	$Pd(PPh_3)_2Cl_2 + Cu(OAc)_2$	232	401	94	96	4
7	$CyNH_2$	CH_3CN	$Pd(PPh_3)_2Cl_2 + Cu(OAc)_2$	286	324	100	92	8
8	$PhCH_2NH_2$	CH_3CN	$Pd(PPh_3)_2Cl_2 + Cu(OAc)_2$	307	283	92	96	4
9	$CH_3(CH_2)_{10}CH_2NH_2$	DMF	$Pd(PPh_3)_2Cl_2 + Cu(OAc)_2$	36	–	82	Trace	42
10	$[(CH_3)_2CH]_2NH$	CH_3CN	$Pd(PPh_3)_2Cl_2 + Cu(OAc)_2$	67	–	–	–	–
11	$NH_2CH_2CH_2NH_2$	CH_3CN	$Pd(PPh_3)_2Cl_2 + Cu(OAc)_2$	231	–	2.8	–	100
12	$NH_2CH_2(CH_2)_4CH_2NH_2$	CH_3CN	$Pd(PPh_3)_2Cl_2 + Cu(OAc)_2$	15	–	4.5	–	100
13	$NH_2CH_2(CH_2)_4CH_2NH_2$	MeOH	$Pd(PPh_3)_2Cl_2 + Cu(OAc)_2$	67	–	98	–	17

[a] Current efficiency (CE) = yield of dialkylurea (mol) × 2/(charge/96,500).

indicated that depending on different aliphatic amines, varied conversion and selectivity were achieved, except for entry 10 in which no conversion could be observed. There were only two products which were formed during the electrocatalytical carbonylation of aliphatic mono-amines, i.e. dialkylurea and isocyanate. When *n*-$BuNH_2$ was used as the substrate, $Cu(OAc)_2$ exhibited moderate catalytic activity (entry 1). This was not consistent with the result obtained by Hartstock et al. [19], who reported that $Cu(OAc)_2$ acted only as an electron transfer agent. Better conversion and selectivity for desired products were obtained when only $PdCl_2$ was used as catalyst (entry 2). However, both of the catalytic activity and selectivity were greatly increased further when $Pd(OAc)_2$ (entry 3) and $Pd(PPh_3)_2Cl_2$ (entry 4) together with $Cu(OAc)_2$ were, respectively, used as catalysts, and almost 100% conversion and 98% selectivity were achieved in the case of $Pd(PPh_3)_2Cl_2 + Cu(OAc)_2$. This indicated that there may exist synergism between Pd(II) and Cu(II) which could enhance the catalytic performance for the carbonylation of the aliphatic amines into the dialkylureas.

Since $C_{12}H_{25}NH_2$ was not dissolved in CH_3CN, DMF was used as solvent for its carbonylation reaction (entry 9). Although, 82.1% of $C_{12}H_{25}NH_2$ was converted, only trace amount of dialkylurea was formed and the main products in selectivity were $C_{12}H_{25}NCO$ (41.5%), $C_{12}H_{25}CONH_2$ (38.7%), and $(C_{12}H_{25})_2NH$ (19.7%), respectively. The production of $(C_{12}H_{25})_2NH$ may be due to the cleavage of C–N bond of $C_{12}H_{25}NH_2$ and further reaction of resulting species in DMF.

It can be also seen that the carbonylation was affected by the molecular structure of the amine. The conversion of *t*-$BuNH_2$ was obviously low probably due to the steric crowding around the N atom, and the steric crowding around the N atom in the molecule of $[(CH_3)_2CH]_2NH_2$ was so enormous that no conversion could be observed (entry 10).

For diamines, the conversion was low under the same reaction conditions (entries 11–13). No dialkylurea could be found and the only product was the corresponding diisocyanate and there were no other detectable by-products. Also, the solvent has strong influence on the selectivity of the product. When methanol was used as solvent (entry 13), the conversion was greatly enhanced. However, in addition to the formation of hexane diisocyanate, the major products were C_6 and C_7 aliphatic esters and acids (ca. 83% in selectivity) because of the cleavage of C–C and C–N bond of the diamines and further reaction of resulting species in methanol. It is interesting to mention that there was no formation of the corresponding carbamate during the reaction, although methanol was used as solvent.

During each reaction, the passed current, depending on the substrate, was gradually decreased from the initial ca. 15 mA to the final ca. 0.2 mA. It seems that there was no relationship between the charge consumed and the conversion of substrate. Assuming the electrocatalytic carbonylation, the reaction can be written simply as

$$2RNH_2 + CO \rightarrow RNHCONHR + 2H^+ + 2e^- \qquad (2)$$

It can be seen that current efficiency of dialkylurea formation was greater than 100%, reaching the maximum of 401%. It could be conjectured that there may also exist a non-Faradic electrochemical modification of catalytic activity in this homogeneous electrocatalytical system, which was observed in heterogeneous electrocatalytic system previously [20,21]. Although, the detailed mechanism is not clear at this stage, the experimental results suggested that $Cu(OAc)_2$ acted as not only an electron transfer agent but also a catalyst.

4. Conclusions

This electrocatalytical carbonylation offers an advantage over the traditional heterogeneous and homogeneous oxidative carbonylation of amines in that it does not need drastic reaction conditions to produce high yields while avoiding the use of dangerous CO/O_2 gas mixture. The catalytic media and reaction conditions used in this work could be optimized further. To the best of our knowledge, it is the first time that the syntheses of several dialkylureas by indirect electrocatalytical carbonylation of corresponding aliphatic amines were performed through a Pd and Cu complex catalyst system under mild conditions, and that a non-Faradic electrochemical modification of homogeneous electrocatalytic activity was observed. The details of this phenomenon are now the subject of our further research work.

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