Electrochemical activation of carbon dioxide: synthesis of carbamates†

Maria A. Casadei,[a] Achille Inesi,[b] Franco Micheletti Moracci[a] and Leucio Rossi*[b]

[a] *Dipartimento di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università di Roma 'La Sapienza', P.le Aldo Moro 5, I-00185 Roma, Italy*
[b] *Dipartimento di Chimica, Ingegneria Chimica e Materiali, Università de L'Aquila, I-67040, Monteluco di Roio, L'Aquila, Italy*

Electrochemically activated CO_2 reacts with amines and EtI under mild reaction conditions affording the corresponding carbamates in high to excellent yields.

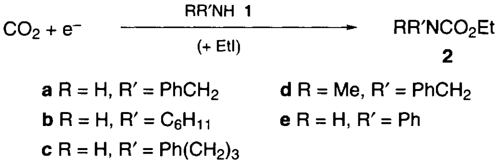
In recent years a great deal of effort has been devoted to the study of the activation of carbon dioxide in order to utilise it as a source of carbon in organic synthesis.[1]

The activation of CO_2, carried out by electrochemical reduction, has been described as a monoelectronic process yielding the radical anion $CO_2^{\cdot-}$ which, in aprotic solvent, evolves to oxalate, carbonate and formate.[2] The oxalate : carbonate ratio is affected by several factors including the nature of the electrodic material, solvent and supporting electrolyte, CO_2 concentration, temperature and current density.[3] Formate is produced only in the presence of residual water. However, the practical use of the direct activation of CO_2 is strongly hindered by its reduction potential, which precludes its use in the presence of many organic substrates containing easily reducible functional groups.

Organic carbamates are compounds of growing interest because of their many applications[4] and, in addition to the classical 'phosgene routes', new interesting methods for their synthesis have been recently proposed. Toxic and harmful reagents as phosgene and isocyanates have been replaced with carbon dioxide and organic carbonates.[5] Here we report a simple electrochemical methodology for the synthesis of carbamates **2** starting from aliphatic and aromatic amines **1** and carbon dioxide. It relies upon the activation of CO_2 obtained by direct reduction (Scheme 1), and overcomes the drawbacks mentioned.

A solution of MeCN–Et_4NClO_4 (TEAP; 0.1 mol dm^{-3}), with continuous CO_2 bubbling, was electrolysed at a potential (−2.1 V *vs.* SCE) that allows the reduction of CO_2 to $CO_2^{\cdot-}$. At the end of the electrolysis, after bubbling N_2 and then adding EtI as alkylating reagent, diethyl oxalate, diethyl carbonate and traces of ethyl formate were formed, in agreement with previous literature data.[3] When the electrolysis was repeated on a solution initially also containing benzylamine, the carbamate **2a** and diethyl oxalate were formed, while no trace of diethyl carbonate was found (procedure A).

The same results (with better yields of carbamate) were obtained if benzylamine was added at the end of the electrolysis, after bubbling N_2, but an hour before the addition of EtI (procedure B). On the contrary, if the amine was added after EtI, the yield of carbonate increased at the expense of carbamate (procedure C). When the delay between the addition of EtI and the amine was longer than 50 min, carbamate was completely absent.



$$CO_2 + e^- \xrightarrow[\text{(+ EtI)}]{RR'NH\ \mathbf{1}} RR'NCO_2Et\ \mathbf{2}$$

a R = H, R′ = $PhCH_2$
b R = H, R′ = C_6H_{11}
c R = H, R′ = $Ph(CH_2)_3$
d R = Me, R′ = $PhCH_2$
e R = H, R′ = Ph

Scheme 1

With procedure B seemingly the most promising, electrolyses using this method were carried out using **1a** as a model compound and changing the nature of the electrode and the amount of the electricity supplied to the system. Both parameters have remarkable effects on the yield of **2a**, as shown in Fig. 1.

To test the effectiveness and generality of the methodology, electrolyses were also carried out under optimised conditions (Cu cathode, 3 F mol^{-1} of **1**)‡ by varying the nature of the substrate (Table 1, entries 1 and 7–10), the solvent (entry 2), the supporting electrolyte (entry 3), and under galvanostatic control

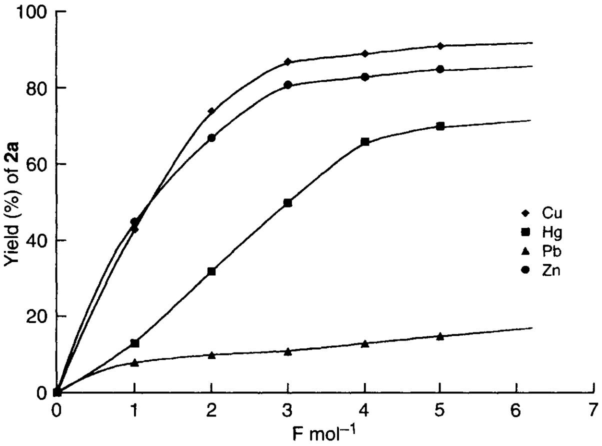


Fig. 1 Synthesis of **1a** from **2a** according to procedure B: effect of cathode material

Table 1 Synthesis of carbamates **2** from amines **1** and CO_2

Entry	Amine **1**	SSE[a]	Potential or current density[b]	Yield of **2** (%)[c]
1	**a**	A	−2.1 V	**a** (89)
2	**a**	B	−2.1 V	**a** (83)
3	**a**	C	−2.1 V	**a** (88)
4	**a**	A	2 mA cm^{-2}	**a** (92)
5	**a**	A	4 mA cm^{-2}	**a** (86)
6	**a**	A	8 mA cm^{-2}	**a** (83)
7	**b**	A	−2.1 V	**b** (93)
8	**c**	A	−2.1 V	**c** (73)
9	**d**	A	−2.1 V	**d** (98)
10	**e**	A	−2.1 V	**e** (63)

[a] Solvent–Supporting electrolyte system: A = MeCN–0.1 mol dm^{-3} Et_4NClO_4; B = DMF–0.1 mol dm^{-3} Et_4NClO_4; C = MeCN–0.1 mol dm^{-3} Et_4NBF_4. [b] Divided cell, Cu cathode, Pt anode. [c] Analyses after 3.0 F mol^{-1} of **1**; yields based on the starting amine **1** refer to the isolated carbamate ester.

(entries 4–6): in all the cases, high to excellent yields of carbamates were obtained (Table 1).

Footnotes

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‡ *General Procedure*: The electrolyses were carried out at −2.1 V (or at the indicated current density) in MeCN–TEAP (20 ml, 0.1 mol dm^{-3}) with continuous CO_2 bubbling. At the end of the electrolyses (3 F mol^{-1} of **1**), N_2 was bubbled through the solution for 10 min and the amine (1.0 mmol) was added. The solution was stirred at room temperature for 60 min (the disappearance of the amine was monitored by TLC). Subsequently, a fivefold molar excess of EtI was added and the solution was stirred overnight at room temperature. The solvent was then removed under reduced pressure and the residue extracted with Et_2O. The extracts were dried and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography affording pure carbamate.

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