Novel Electrochemical Reactivity of Ni(cyclam)Br$_2$: Catalytic Carbon Dioxide Incorporation into Epoxides

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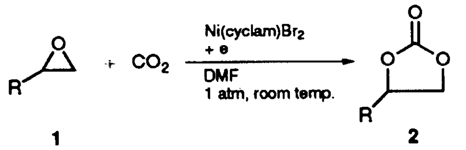
Cyclic carbonates are obtained in good yields from terminal epoxides and carbon dioxide in an electrochemical nickel-catalysed reaction.

The coordination chemistry and the electrochemistry of Ni^{II} associated to cyclam-type macrocycles (cyclam = 1,4,7,11-tetraazacyclotetradecane) is a topic of current interest due to the applications of such complexes as catalysts for oxidation[1] and reduction reactons.[2] The reductive electrochemistry of Ni^{II}-(cyclam) complexes has been shown to proceed *via* a one-electron reduction to Ni^{I}(cyclam) intermediates.[3] Complexes of Ni^{II} with cyclam derivatives have been reported to catalyse the electrochemical reductive dimerization of organic halides[4] and more recently, examples of intramolecular electroreductive cyclization of unsaturated vinyl or aryl halides with related complexes have been described.[5,6] However, for most of these reactions, the parent complex Ni^{II}(cyclam) was inefficient as a catalyst, and related alkyl or unsaturated derivatives had to be used as ligands for nickel. On the other hand, Ni^{II}(cyclam) perchlorate has been described as an efficient catalyst for the electroreduction of carbon dioxide into carbon monoxide.[7,8]

During the course of our studies directed toward the nickel-catalysed activation and incorporation of carbon dioxide into organic substrates[9,10] we found a novel electrochemical reaction: the catalysis by Ni(cyclam)Br$_2$ of carbon dioxide incorporation into terminal epoxides to afford cyclic carbonates [eqn. (1)].



(1)

Cyclic carbonates present interesting applications as polar aprotic solvents and as precursors for polycarbonates and other polymeric materials.[11] Moreover, the use of CO$_2$ as a C$_1$ building block in organic synthesis is important as a phosgene replacement agent. New processes involving carbon dioxide are of special interest if new carbon–carbon bond-forming reactions can be performed catalytically.[12]

The synthesis of carbonates from epoxides and CO$_2$ can be brought about in the presence of alkali salts (and a cocatalyst)[13] or an ammonium or phosphonium salt,[14] generally under high CO$_2$ pressure and elevated temperatures. Catalysis by transition metal complexes has also been reported in the case of Cu^{I},[15] Ni^{0} [16] and Ti^{III} [17] complexes, under 6–35 atm CO$_2$ pressure and at 100–125 °C.

To our knowledge, no report in the literature deals with the electrochemical functionalization of epoxides with carbon dioxide to form carbonates in catalysed or uncatalysed reactions. The electrochemical procedure for the synthesis of cyclic carbonates presented here takes place under very mild conditions: room temperature and atmospheric CO$_2$ pressure. The electrosyntheses are carried out in a single-compartment cell fitted with a consumable anode. The use of sacrificial anodes in preparative scale electrolyses has demonstrated its efficiency in several synthetic applications.[18,19] The method is also compatible with transition metal complexes as the catalysts.[9,20]

In the presence of Ni(cyclam)$^{2+}$ complex, the reactions at the electrodes are; at the anode (generally a magnesium rod), the oxidation of the metal; and at the cathode, the reduction of the nickel(II) complex,[3] leading to Ni^{I}(cyclam)$^{+}$ [eqns. (2) and (3)].

$$\text{Anode: Mg} \rightarrow \text{Mg}^{2+} + 2e^- \qquad (2)$$

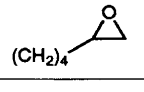
$$\text{Cathode: Ni(cyclam)}^{2+} + e^- \rightarrow \text{Ni}^{I}\text{(cyclam)}^{+} \qquad (3)$$

Preliminary electrocarboxylation tests were carried out with styrene oxide **1a** as the model compound. The electrolysis of **1a** in DMF as the solvent and potassium bromide as the supporting electrolyte, in the presence of a catalytic amount of Ni-(cyclam)Br$_2$ and CO$_2$ (1 atm), with a Mg–carbon fibre couple of electrodes, led to a 64% epoxide conversion (7 h, room temp.), with the formation of phenyl carbonate **2a** in 92% yield (overall yield of 59%). In the absence of electricity no reaction occurred, similarly when the nickel catalyst was absent no carbonate was formed.

The presence of magnesium ions from anodic oxidation are important in controlling carbon dioxide incorporation. Thus, when the electrolysis was carried out in a two-compartment cell, in the absence of Mg^{2+} ions in the cathodic compartment, 77% of the starting epoxide **1a** could be recovered and only 4% of carbonate **2a** was formed. We have already noted the key influence of Mg^{2+} ions for catalysis in the electrocarboxylation of alkynes by nickel–bipyridine complexes,[9] and an example has also been reported in CO$_2$ electroreduction using iron porphyrins.[21]

The influence of the nature of the electrodes was examined in the carboxylation of **1a** (Table 1).† Magnesium and aluminium rods were tested as the sacrificial anodes, and carbon fibre, stainless steel and nickel foam as the cathode materials. The role of the anode can be important for the presence in solution of Mg^{2+} or Al^{3+} ions, as well as to determine the potential range. These Mg^{2+} or Al^{3+} ions, from anodic oxidation are Lewis acids, able to coordinate the oxirane ring. The nature of the cathode, though chemically inert, may strongly influence the carbon dioxide adsorption and reduction by the nickel complex. Our results using a Al anode with several cathodes (carbon fibre, stainless steel, nickel foam) for the electrocarboxylation of **1a**, showed low epoxide conversions (7–20%, 7 h) and low product selectivities (carbonate formation of 30–60% from converted epoxide, with total carbonate yields of 3–6%, see example in Table 1). However, a high selectivity towards **2a** was obtained with a Mg anode. The best yield concerning carbonate

Table 1 Ni(cyclam)Br$_2$ catalysed electrochemical reactivity of epoxides **1** with CO$_2$

Epoxide	R	Anode/cathode	Yield (%)
1a	Ph	Mg/carbon fibre	59
1a	Ph	Mg/nickel foam	66
1a	Ph	Al/stainless steel	6
1a	Ph	Mg/stainless steel	91
1b	CH$_2$Ph	Mg/stainless steel	90
1c	*n*-C$_6$H$_{13}$	Mg/stainless steel	74
1d	*n*-C$_8$H$_{17}$	Mg/stainless steel	60
1e	(CH$_2$)$_4$CH=CH$_2$	Mg/stainless steel	73
1f		Mg/stainless steel	70 (dicarbonate)

formation was achieved with Mg–stainless steel couple of electrodes (92%). Carbon fibre or nickel foam cathodes led to isolated yields of 59 and 66%, respectively, after 7 h, and no significant increase in carbonate yield was observed with longer reaction times. In a 24 h reaction, some product degradation occurred.

The carbon dioxide incorporation into the epoxide ring was examined for a series of terminal epoxides, see Table 1. Aromatic, benzylic, and aliphatic terminal epoxides afforded the corresponding cyclic carbonates with good yields and excellent selectivities, ⩾95%. Oct-7-ene-1,2-epoxide **1e** led to the unsaturated carbonate **2e** without intramolecular cyclization or any modification on the double bond, despite the radical-type intermediates proposed in other Ni^{II}(cyclam) electrochemical processes.[3]

The carboxylation of the diepoxide **1f** enabled the selective preparation of the dicarbonate **2f** in 70% overall yield. No product of single CO_2 insertion was observed (*e.g.* mono-epoxidemonocarbonate). The first carbon dioxide molecule insertion into the first epoxide group may induce the second epoxide carboxylation.

The carbonate formation also takes place when using acetonitrile as the solvent, but the reactions are less selective. Under the same conditions as in Table 1 (Mg–stainless steel electrodes), epoxide **1a** was completely converted and **2a** was obtained in 69% yield.

Ni^{II}(cyclam) in aqueous DMF has been reported to effect the carbon dioxide electroreduction into CO; however, we observed that in the presence of the epoxide, the reactivity of carbon dioxide is modified; the CO_2 reduction is inhibited in favour of its incorporation into the oxirane ring. The inhibition of the carbon dioxide electroreduction favouring C–C bond formation has been reported in alkyne carboxylation catalysed by nickel–bipyridine complexes.[9]

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Footnote

† *General procedure*: the single-compartment electrolysis cell was similar to that described in ref. 18, fitted with a magnesium rod anode and a stainless steel cathode. A freshly distilled DMF (40 ml) solution of Ni(cyclam)Br_2 (0.3 mmol),[22] KBr (0.08 mmol) and the epoxide (3 mmol) was electrolysed under bubbling of carbon dioxide (1 atm) at room temp. with continuous stirring. A current of 60 mA was applied between the electrodes connected to a DC power supply (apparent cathodic current density of 0.25 A dm^{-2}) during 7 h. The current was limited by a maximum applied voltage of 15 V. The reaction mixture was then heated at 50 °C for 12 h. The solution was hydrolysed with 50 ml of 0.1 mol dm^{-3} HCl solution and extracted with Et_2O, the organic layer was washed with H_2O, dried over $MgSO_4$ and concentrated. The cyclic carbonates were isolated by flash chromatography on silica gel eluting with pentane–Et_2O mixtures. The products were analysed by NMR and IR spectroscopy, MS and GLC and compared to authentic samples.

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