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Nickel-catalyzed electrochemical carboxylation of epoxides: mechanistic aspects†

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The electrochemical incorporation of carbon dioxide into epoxides catalyzed by nickel(II) complexes afforded cyclic carbonates in good yields under very mild conditions (p_{CO_2} = 1 atm, room temperature). Mechanistic and electrochemical studies revealed the cooperative role of reduced nickel species in the activation of CO_2 and the influence of magnesium ions as Lewis acids in the activation of the oxirane ring. Both the presence of nickel catalysts and Mg^{2+} ions were necessary for the electrocarboxylation of epoxides under mild conditions.

Keywords: epoxide; carbon dioxide; cyclic carbonate; nickel; magnesium ions; electrochemical; catalysis; carboxylation; mechanism

INTRODUCTION

In the field of carbon–carbon bond formation involving CO_2, we have been interested in the reactivity of epoxides with CO_2 for the synthesis of cyclic carbonates.[1] These are important synthons for the preparation of functionalized organic intermediates, such as 1,2-diols,[2] and for the synthesis of various polymeric materials.[3] Their preparation from CO_2 as a C_1 building block (instead of phosgene) constitutes an interesting alternative based on the use of non-toxic, abundant and cheap starting material.[4]

The reaction of epoxides with CO_2 for the preparation of cyclic carbonates is generally carried out at high temperatures (>100 °C) and elevated CO_2 pressures (>40 atm) in the presence of metal[5] or onium salts[6] as the catalysts. Catalysis by transition metal complexes based on nickel(0),[7] palladium (0),[8] copper(I),[9] titanium(IV)[10] and chromium(III)[11] have also been reported. We have been working on a novel electrochemical method based on the use of nickel(II) catalysts,[1] and we report here our results concerning some chemical, electrochemical and mechanistic aspects of this reaction.

RESULTS AND DISCUSSION

Electrocarboxylations

The electrochemical method allows the efficient transformation of terminal epoxides into cyclic carbonates under very mild conditions, according to

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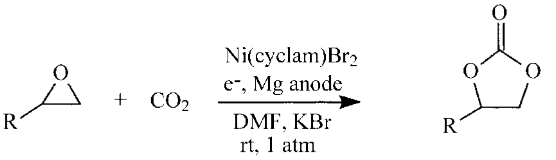
Eqn [1]:



R	Yield (%)
Ph	92
$PhCH_2$	91
$PhOCH_2$	99
nC_6H_{13}	75
nC_8H_{17}	62
$BuOCH_2$	85

The carboxylation was carried out in a single-compartment cell[12] fitted with a magnesium anode and a stainless steel cathode, in DMF, at room temperature and at atmospheric CO_2 pressure. 3 mM of the epoxide and 10 mol% of the catalyst $Ni(cyclam)Br_2$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) were introduced and KBr was used as supporting electrolyte (0.02 M). The electrolyses were performed at a constant current of 60 mA for 7 h. With this approach a broad variety of substituted epoxides were transformed into cyclic carbonates under good yields (Eqn [1]).

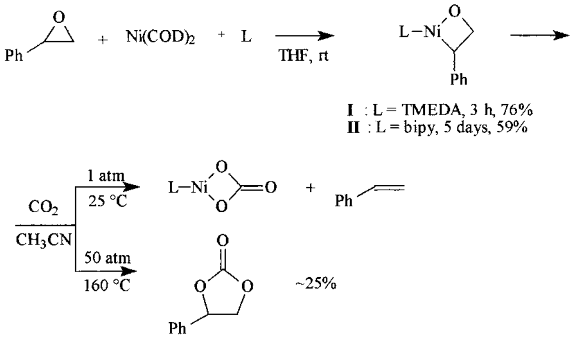
The same electrochemical reaction with styrene oxide was also efficient in the presence of $[Ni(bipy)_3][BF_4]_2$ as pre-catalyst (bipy = 2,2′-bipyridine), leading to the corresponding cyclic carbonate in 80% yield.

In the absence of current, styrene oxide did not react and could be recovered unchanged. In the absence of the nickel(II) complex, styrene oxide yielded the corresponding cyclic carbonate in low yield through a non-selective reaction, in which products from the epoxide ring opening, as well as polymeric compounds, were formed. Oxalate was obtained in this electrolysis, resulting from the reductive dimerization of CO_2.[13]

The nature of the electrodes and of the supporting electrolyte proved to be important factors in the control of the carbonate yield and selectivity. The best conditions for styrene oxide carboxylation with $Ni(cyclam)Br_2$ were found in DMF with Mg/stainless steel as the electrodes couples in the presence of KBr as supporting electrolyte.

Nickelaoxetanes as possible intermediates

From a mechanistic point of view, the reaction of epoxides with CO_2 (under elevated pressures) in the presence of nickel(0)–phosphine complexes has been proposed to proceed through the formation of intermediate nickelaoxetanes.[7] Recently, such metallacycles have been prepared and characterized from $Ni(COD)_2$ in the presence of N-donor ligands such as 2,2′-bipyridine or TMEDA[14] (Scheme 1).



Scheme 1

Complexes **I** and **II** were not stable in air. Their chemical reactions with CO_2 did not allow the synthesis of cyclic carbonates under mild conditions ($p_{CO_2} = 1$ atm, $T = 25$ °C); nickel carbonate and styrene were obtained instead. Styrene carbonate could only be obtained in low yields (*ca* 25%) from **I** or **II** under increased CO_2 pressure and temperature (50 atm, 160 °C, Scheme 1).

The electrochemical reactivity of complexes **I** or **II** with CO_2 under the standard electrochemical conditions also did not produce any cyclic styrene carbonate.

The results from nickelaoxetane reactivity with CO_2 indicate that such metallacycles should not be intermediates in the catalytic electrochemical reaction.

Moreover, without isolation of the nickelaoxetanes, the direct reaction of styrene epoxide with CO_2 in DMF in the presence of 10 mol% of Ni(COD)(bipy) at 50 atm and 25 °C for 3 h led not to styrene carbonate but to the recovery of styrene oxide in 75% yield.

Cyclic voltammetry

The interaction of epoxides and CO_2 with $Ni(cyclam)Br_2$ was examined by cyclic voltammetry. Figure 1 presents the behaviour of the nickel complex in a DMF solution containing tetrabutylammonium tetrafluoroborate at room temperature (curve a). A reversible, one-electron reduction peak of nickel(II) to nickel(I) was observed at −1.45 V *vs* Ag/AgCl, in agreement with the literature.[15]

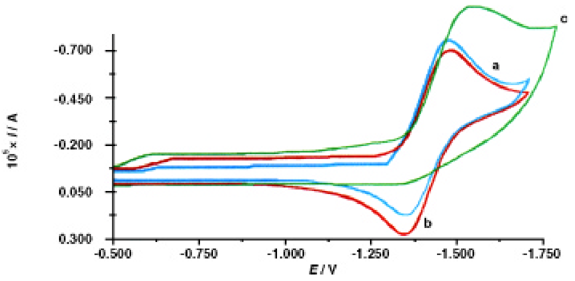


Figure 1 Cyclic voltammetry on a platinum electrode, at 100 mV s^{-1} and room temperature, of a DMF solution of n-$Bu_4N^+BF_4^-$ (0.1 M), reference electrode Ag/AgCl. (a) Ni(cyclam)Br_2, 2.5 mM; (b) after addition of ten equivalents of styrene epoxide; (c) after saturation with CO_2 at 1 atm.

In the presence of from 0.5 to 10 equivalents (Fig. 1, curve b) of styrene oxide no significant changes of the initial nickel(II) reduction curve could be observed. The absence of any modification of the nickel(II)/nickel(I) system indicates that there is no strong interaction and no rapid chemical reaction between the epoxide and the electrogenerated nickel(I) complex.

In the presence of CO_2 (saturated solution at atmospheric pressure) the cyclic voltammogram presents an irreversible nickel(II)/nickel(I) transition (Fig. 1, curve c), the sign of a rapid coordination and further reactivity of electrochemically generated nickel(I) with CO_2. The same behaviour (Fig. 1, curve c) was obtained in the absence of the epoxide.

The electrochemical behaviour of Ni(cyclam)$^{2+}$-type complexes with CO_2 in aqueous media (or in H_2O–DMF mixtures) has been reported to present an intense catalytic wave corresponding to the CO_2 electroreduction into CO in the presence of protons.[16]

In anhydrous DMF (Fig. 1, curve c), a slightly higher intensity than for curve a is presented, but there is no strong catalytic phenomena of CO_2 electroreduction.

The cyclic voltammogram of $[Ni(bipy)_3][BF_4]_2$ in the presence of epoxide and CO_2 in a DMF solution was also examined. The addition of styrene oxide (0.5 to 10 equivalents) to an $[Ni(bipy)_3]$ $[BF_4]_2$ solution did not modify the cyclic voltammetry behaviour of the initial nickel(II)/nickel(0) reversible reduction at -1.15 V *vs* Ag/AgCl.[17] In the presence of CO_2 a catalytic wave appeared at -1.6 V, corresponding to the CO_2 electroreduction, in agreement with the literature.[16] We can conclude that at the time scale of the cyclic voltammetry, styrene oxide does not interact strongly with nickel(II) or with electrogenerated $Ni^I(cyclam)^+$ or nickel(0)–$(bipy)_2$-type complexes. In contrast, both reduced metal species present a strong interaction with CO_2. This electrochemical behaviour is in agreement with the low chemical reactivity of styrene oxide with CO_2 in the presence of nickel(0)–amine complexes under mild conditions in which no styrene carbonate was obtained.

In contrast, the cyclic voltammogram of complex **I** did not present any electroactivity from 0 to -2 V *vs* Ag/AgCl. In the presence of CO_2, an irreversible peak appeared at -1.5 V, which was assigned to the reduction of (TMEDA)Ni(carbonate), according to Scheme 1.

Influence of metal salts

In contrast to the low chemical reactivity of nickel(0) towards the insertion of CO_2 into epoxides, electrogenerated nickel(0) or nickel(I) complexes were shown to be efficient catalysts in the electrochemical carboxylation of such substrates to cyclic carbonates under mild conditions (Eqn [1]).

However, in the presence of metal salts and high CO_2 pressures, cyclic carbonate formation from epoxides has been proposed to proceed through oxirane ring opening followed by reaction with CO_2 and ring closure.[5]

In the electrochemical reaction of epoxide carboxylation, besides the nickel(II) catalyst, the reaction medium also contains KBr as supporting electrolyte and Mg^{2+} ions, formed progressively from the anodic oxidation of the magnesium rod anode. We examined the effect of both KBr and $MgBr_2$ in the reaction of styrene oxide with CO_2. Table 1 presents the results from the influence of the CO_2 pressure on the yield and selectivity of the cyclic carbonate formation in the presence of KBr or $MgBr_2$ (30 mol% with respect to the epoxide) in chemical reactions in DMF at 20 °C for 3 h.

With KBr, under atmospheric CO_2 pressure, no carbonate was formed. Only at a pressure of 50 atm was the epoxide conversion attained in 80% yield.

In similar reactions in the presence of anhydrous $MgBr_2$ (prepared electrochemically from dibromoethane with an Mg anode) the epoxide conversion was of 80% at atmospheric CO_2 pressure, with a carbonate yield of 46% (bromoalcohol and polymeric materials were also obtained). Yields and selectivity of cyclic carbonate increased with the CO_2 pressure.

Magnesium ions seem to play an important role

Table 1 Influence of the CO_2 pressure on the reaction with styrene oxide for the synthesis of styrene carbonate in the presence of a metal salt MX[a]

MX (30 mol%)	CO_2 pressure (atm)	Epoxide conversion (%)	Carbonate yield (%)[b]
KBr	1	—	—
KBr	10	12	99
KBr	50	80	99
$MgBr_2$	1	80	46
$MgBr_2$	10	90	74
$MgBr_2$	50	99	96

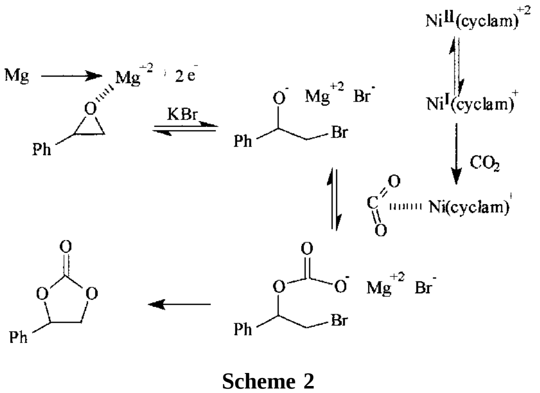
[a] Reactions carried out at a 3 mmol scale in DMF at room temperature for 3 h.
[b] Yield based on converted epoxide.

as Lewis acids in the epoxide carboxylation process under mild conditions. However, the reaction in the presence of $MgBr_2$ at atmospheric pressure but in the absence of a nickel catalyst exhibited poor selectivity (Table 1).

In agreement with these results, we propose a mechanism for the electrochemical CO_2 incorporation into epoxides with a cooperative effect of both Mg^{2+} ions and reduced nickel species (Scheme 2).

The proposed mechanism involves the epoxide ring opening mediated by $MgBr_2$, forming a magnesium bromoalcoholate. In a parallel process, the electrochemical reductive medium generates reduced $Ni(0)(bipy)_2$ or Ni(I)(cyclam) species from the corresponding Ni(II) complexes, able to coordinate CO_2. The bromoalcoholate reacts with the activated CO_2 to form an intermediate Mg^{2+} carbonate, which then undergoes ring closure to the cyclic carbonate.

In conclusion, the cooperation of Mg^{2+} ions in the Lewis acid activation of the epoxide for its ring opening with the reduced, electrogenerated nickel species that activate CO_2 may explain the efficient and high yield formation of cyclic carbonates by the electrochemical method under very mild conditions, compared with two other processes of epoxide carboxylation reported.



Scheme 2

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