ChemComm
www.rsc.org/chemcomm

Electrocatalytic carboxylation of benzyl chlorides at silver cathodes in acetonitrile

Abdirisak A. Isse and Armando Gennaro*
Dipartimento di Chimica Fisica, Università di Padova, via Loredan 2, 35131 Padova, Italy.
E-mail: A.Gennaro@chfi.unipd.it; Fax: +39 049 8275135; Tel: +39 049 8275132

Received (in Cambridge, UK) 11th July 2002, Accepted 8th October 2002
First published as an Advance Article on the web 24th October 2002

Silver exhibits powerful electrocatalytic activities towards the reductive carboxylation of benzyl chlorides (RCl): in CO_2-saturated CH_3CN, reduction of RCl occurs at potentials that are about 0.6 V more positive than those of the same process at Hg or carbon electrodes and gives carboxylic acids in good to excellent yields.

The electrochemical reduction of benzyl chlorides in CO_2-saturated solvents has been extensively investigated as a synthetic route to carboxylic acids.[1] In fact, this method of synthesis may provide a valuable alternative route to the manufacture of 2-arylpropanoic acids, which are of great interest in the pharmaceutical industry.[2] A drawback to the use of benzyl chlorides as starting material is, however, that their reduction at the most commonly used cathodes occurs at very negative potentials, where concomitant reduction of CO_2 may take place, resulting in undesired products and a decrease of current efficiency. This has prompted the search for suitable catalytic systems capable of mediating the electrocarboxylation process.

Several nickel and palladium complexes with phosphine ligands,[3] as well as some square-planar cobalt[4] and nickel[5] complexes, have been used as homogeneous catalysts for the electrochemical carboxylation of various benzyl chlorides. Electrogenerated organic radical anions, acting as outer sphere electron transfer agents, have also been used.[5,6] Although good current efficiencies were obtained with many of these catalytic systems, only moderate to low turnover numbers were achieved. A high turnover number has been reported only in one case where a zeolite-encapsulated cobalt complex was used.[4c]

A very interesting type of catalysis in electrochemistry is one in which the electrode, besides being a source or a sink for electrons, behaves as a catalyst for the redox reaction. Several electrode materials, *e.g.*, Pt, Ni, Au, stainless steel and graphite, have been used for the electrocarboxylation of benzyl chlorides. Although the role of the cathode was not investigated in depth, it seems that none of the electrodes so far tested has a particular electrocatalytic effect towards the reductive carboxylation of the halides. Very recently, a series of papers dealing with the reduction of organic halides at silver cathodes has appeared.[7] The most important result emerging from such studies is that silver exhibits extraordinary electrocatalytic activities towards the reduction process, especially in the case of bromides and iodides. With the exception of a study on the carboxylation of some aromatic halides, which gave only poor to moderate yields,[8] the possibility of exploiting the electrocatalytic nature of silver in electrocarboxylations has not been explored yet.

Here we report the results of an investigation on the potentialities of silver as an electrocatalyst in the carboxylation of benzyl chlorides. The process was studied in CH_3CN + 0.1 M Et_4NClO_4 at Ag, Hg and carbon cathodes at 25 °C.[9] Two types of silver electrode were used: one made from the bulk metal and the other (denoted Ag/Pt) prepared by electrodeposition of Ag on Pt. On all three electrodes, a single irreversible peak is observed in cyclic voltammetry. Fig. 1 shows cyclic voltammograms recorded at Ag for the reduction of $PhCH_2Cl$ in the absence and presence of CO_2, as well as for the reduction of CO_2 alone. It is noteworthy that E_p of $PhCH_2Cl$ is about 0.5 V more positive than that of CO_2 and becomes even more positive when the solution is saturated with CO_2. Voltammograms similar to those shown in Fig. 1 were obtained for all benzyl chlorides (RCl). The position of the peak, however, depends strongly on the electrode material. The data obtained at Ag, Hg and glassy carbon (GC) electrodes are collected in Table 1. The data obtained on Ag/Pt (not shown in the Table) were the same, within experimental error, as those reported for Ag. Whereas the presence of CO_2 had no effect on the peak potential (E_p) of RCl at GC or Hg, significant positive shifts were observed at the silver electrodes. The last column shows E_p values obtained at Ag in CO_2-saturated CH_3CN.

Electron transfer to organic halides, RX, involves rupture of the carbon–halogen bond.[10] The electrode may get involved in interactions with RX or its reduction intermediates and products. Because of its inertness to the species involved in the reaction, GC has been suggested as the best electrode material for the investigation of the reduction mechanism of organic halides. We may, therefore, use this electrode as a reference material to examine the electrocatalytic properties of the electrodes towards the reduction of RCl. The data reported in Table 1 show that similar E_p values were obtained at GC and Hg, suggesting that, for both electrodes, surface processes do not play an important role in the reaction.[11] Instead, the E_p values obtained at Ag are considerably more positive than those measured at GC. Such a great difference of E_p between the two

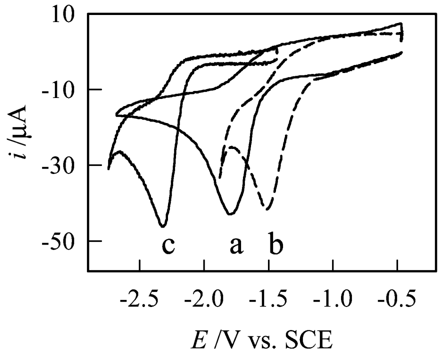

Fig. 1 Cyclic voltammograms recorded at 0.2 V s^{-1} in CH_3CN + 0.1 M Et_4NClO_4 at a Ag electrode. (a) 3 mM $PhCH_2Cl$, (b) as (a) + 0.28 M CO_2, (c) 4 mM CO_2.

Table 1 Voltammetric data for the reduction of benzyl chlorides (3 mM) and CO_2 (4 mM) in CH_3CN + 0.1 M Et_4NClO_4 at v = 0.2 V s^{-1}

	GC	Hg	Ag	
Compound	E_p/ V *vs.* SCE	E_p/ V *vs.* SCE	E_p/ V *vs.* SCE	E_p (CO_2)[a]/ V *vs.* SCE
CO_2	−2.41	−2.46	−2.34	
$PhCH_2Cl$	−2.25	−2.27	−1.79	−1.52
4-$CF_3C_6H_4CH_2Cl$	−1.99	−1.97	−1.67	−1.48
4-$CH_3OC_6H_4CH_2Cl$	−2.26	−2.31	−1.82	−1.52
$PhCH(CH_3)Cl$	−2.23	−2.29	−1.81	−1.53

[a] In the presence of 0.28 M CO_2.

DOI: 10.1039/b206746c

electrodes points to a significant electrocatalytic effect of the silver electrode towards the reduction of RCl.

The extraordinary electrocatalytic effect of Ag is probably related to the high affinity of the metal for halide ions, which is well documented in the literature.[12] As reported earlier for various alkyl halides,[7b,d] it is very likely that reduction of RCl at Ag involves interaction of both RCl and its reduction intermediates and products with the electrode. Such interactions can affect both the thermodynamics and kinetics of the process. Although adsorption of the products has a thermodynamic advantage resulting in a positive shift of the reduction potential, kinetic effects probably play a major role in the electrocatalytic process. In fact, interaction of RCl with Ag with the formation of an activated complex of the form R···Cl···Ag may decrease significantly the great overpotential associated with the dissociative reduction of the carbon–halogen bond.

The most relevant outcome of the voltammetric investigation is that, at Ag cathodes, reduction of RCl occurs at potentials considerably more positive than E_p of CO_2. In the least favourable case, the difference between E_p of CO_2 and that measured for RCl in the presence of CO_2 is 0.51 V (Table 1). This provides a potential window save enough for electrocarboxylation of RCl to be performed without any interference from reduction of CO_2. Controlled-potential electrolyses were carried out in CO_2-saturated solutions containing *ca*. 50 mM RCl (1 mmol) in an undivided cell with an Al sacrificial anode. Both Ag and Ag/Pt electrodes were used. Also some experiments were performed at Hg and graphite electrodes for comparison. In each case, the electrolysis was carried out at a potential just beyond E_p of RCl and was stopped after total conversion of the halide was achieved. At the end of the electrolysis, identification and quantification of the products was done by HPLC. The results are reported in Table 2. The principal product was always the corresponding carboxylic acid (RCO_2H) although its yield depends, to some extent, on the experimental conditions. At silver electrodes, whether bulk or coated on Pt, excellent results both in terms of chemical yields and current efficiencies were obtained.[13] Substituents on the phenyl ring do not strongly modify the product distribution, although, as a general trend, the yield of RH increases with the electron-donating power of the substituent. At graphite and Hg electrodes (entries 4, 5 and 10), poor current efficiencies ($<50\%$) were obtained. Owing to the very negative potentials required for the reduction of RCl at these electrodes, concomitant reduction of CO_2 to give oxalate, CO and carbonate, as previously reported,[14] probably takes place resulting in a high consumption of charge.

In conclusion, we have shown that electrocarboxylation of benzyl chlorides can be successfully achieved without resorting to the use of homogeneous catalysts. The process at Ag cathodes occurs at potentials similar to, or even more positive than, those of the most efficient catalysts so far reported[3–5] and gives carboxylic acids in very high yields without passivation of the electrode. Silver has shown good catalytic properties in the electroreduction of a variety of organic halides and it is fairly likely to be a good cathode material for their electrocarboxylation. The excellent results reported here for the benzyl chlorides recommend a broad research in that direction.

Table 2 Electrocarboxylation of RCl in CH_3CN + 0.1 M Et_4NClO_4

					Product yields[c] (%)	
Entry	RCl	Cathode	E_{app}[a]	n[b]	RH	RCO_2H
1	$PhCH_2Cl$	Ag	−1.65	2.11	6	94
2[d]	$PhCH_2Cl$	Ag	−1.65	2.00	18	53
3	$PhCH_2Cl$	Ag/Pt	−1.65	2.01	5	90
4	$PhCH_2Cl$	C	−2.30	4.49	16	81
5	$PhCH_2Cl$	Hg	−2.24	3.70	4	90
6	$4\text{-}CF_3C_6H_4CH_2Cl$	Ag	−1.55	2.32	2	95
7	$4\text{-}CH_3OC_6H_4CH_2Cl$	Ag	−1.70	2.26	16	79
8	$PhCH(CH_3)Cl$	Ag	−1.68	2.01	15	80
9	$PhCH(CH_3)Cl$	Ag/Pt	−1.68	2.00	6	81
10	$PhCH(CH_3)Cl$	C	−2.29	5.59	14	82

[a] Applied potential (V *vs.* SCE). [b] e⁻ per molecule of RCl. [c] Yield = 100 × (moles of product/moles of RCl). [d] A two-compartment cell was used; 10% benzyl phenylacetate, which accounts for 20% of the starting RCl, was also obtained.

This work was supported by the Consiglio Nazionale delle Ricerche (CNR) and the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR).

Notes and references

1 G. Silvestri, S. Gambino, G. Filardo and A. Gulotta, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 979; O. Sock, M. Troupel and J. Perichon, *Tetrahedron Lett.*, 1985, **26**, 1509; J. Chaussard, M. Troupel, Y. Robin, G. Jacob and J. P. Juhasz, *J. Appl. Electrochem.*, 1989, **19**, 345; A. Sasaki, H. O. Kudoh, H. Senboku and M. Tokuda, in, *Novel Trends in Electroorganic Synthesis*, ed. S. Torii, Springer, Tokyo, 1998, p. 245.

2 J. D. Genders and D. Pletcher, *Chem. Ind.*, 1996, 682.

3 J. F. Fauvarque, A. Jutand and M. Francois, *New J. Chem.*, 1986, **10**, 119; J. F. Fauvarque, A. Jutand and M. Francois, *J. Appl. Electrochem.*, 1988, **18**, 109; J. F. Fauvarque, Y. de Zelicourt, C. Amatore and A. Jutand, *J. Appl. Electrochem.*, 1990, **20**, 338; J. Damodar, S. R. K. Mohan and S. R. J. Reddy, *Electrochem. Commun.*, 2001, **3**, 762.

4 (*a*) C. Folest, J. M. Duprilot, J. Perichon, Y. Robin and J. Devynck, *Tetrahedron Lett.*, 1985, **26**, 2633; (*b*) A. A. Isse, A. Gennaro and E. Vianello, *J. Chem. Soc., Dalton Trans.*, 1996, 1613; (*c*) A. A. Bessel and D. R. Rolison, *J. Am. Chem. Soc.*, 1997, **119**, 12673; (*d*) G. Zheng, M. Stradiotto and L. Li, *J. Electroanal. Chem.*, 1998, **453**, 79; (*e*) W.-H. Chung, P. Guo, K.-Y. Wong and C.-P. Lau, *J. Electroanal. Chem.*, 2000, **486**, 32.

5 A. Gennaro, A. A. Isse and F. Maran, *J. Electroanal Chem.*, 2001, **507**, 124.

6 O. Scialdone, G. Filardo, A. Galia, D. Mantione and G. Silvestri, *Acta Chem. Scand.*, 1999, **53**, 800.

7 (*a*) S. Rondinini, P. R. Mussini, G. Sello and E. Vismara, *J. Electrochem. Soc.*, 1998, **145**, 1108; (*b*) S. Rondinini, P. R. Mussini, F. Crippa and G. Sello, *Electrochem. Commun.*, 2000, **2**, 491; (*c*) S. Rondinini, P. R. Mussini and M. Specchia, *J. Electrochem. Soc.*, 2001, **148**, D102; (*d*) S. Rondinini, P. R. Mussini, P. Muttini and G. Sello, *Electrochim. Acta*, 2001, **46**, 3245.

8 C. L. Scortichini and S. J. Babinec, *J. Electroanal. Chem.*, 1994, **379**, 111.

9 For voltammetric investigations a silver disk of ~0.5 mm diameter, a Pt sphere coated with silver, a glassy carbon disk of ~3 mm diameter and a Hg sphere were used. Before use, the Ag and GC disks were polished with a 0.25 μm diamond paste and ultrasonically rinsed in CH_3CN and ethanol, respectively. For macro-scale electrolyses a Ag foil (12 cm^2), a Hg pool (8 cm^2), a compact graphite rod (6 cm^2) and a Ag-coated Pt plate (2.2 cm^2) were used; the thickness of the Ag film on the latter was ~30 μm. The preparation of the Hg microelecrode and the Ag-coated Pt electrodes was based on electrodeposition of Ag on Pt from aqueous $KAg(CN)_2$ solutions, as previously described.[9a] (*a*) A. A. Isse, A. Gennaro and E. Vianello, *J. Electroanal. Chem.*, 1998, **444**, 241.

10 See, for example, J.-M. Savéant, in, *Advances in Electron Transfer Chemistry*, ed. P. S. Mariano, JAI press, Greenwich, 1994, vol. 4, p. 53 and the references cited therein.

11 The reduction of many organic halides, especially bromides and iodides, at Hg involves organomercury compounds arising from adsorption of the intermediate radicals on the electrode, see: D. G. Peters, in, *Organic Electrochemistry*, eds. H. Lund and M. M. Baizer, Dekker, New York, 1991, p. 361.

12 See, for example, G. Valette, A. Hamelin and R. Parsons, *Z. Phys. Chem.*, 1978, **113**, 71; M. J. Weaver, J. T. Hupp, F. Barz, J. G. Gordon and M. R. Philpott, *J. Electroanal. Chem.*, 1984, **160**, 321; M. L. Foresti, M. Innocenti, F. Forni and R. Guidelli, *Langmuir*, 1998, **14**, 7008; J. E. Pemberton and A. Shen, *Phys. Chem. Chem. Phys.*, 1999, **1**, 5671.

13 An exception is when the experiment was conducted in a divided cell (entry 2). In that case, only a moderate yield of phenylacetic acid was obtained together with $PhCH_2CO_2CH_2Ph$ arising from esterification of the carboxylate with $PhCH_2Cl$. Owing to the stabilisation of the carboxylate ions by the Al^{3+} cations arising from the dissolving anode, the undesirable esterification reaction is avoided when an undivided cell is used.

14 S. Ikeda, T. Takagi and K. Ito, *Bull Chem. Soc. Jpn.*, 1987, **60**, 2517; A. Gennaro, A. A. Isse, M.-G. Severin, E. Vianello, I. Bhugun and J.-M. Savéant, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 3963.