Silver Cathodes as Electrocatalysts in the Carboxylation of Benzyl Chlorides - A.A. Isse and A. Gennaro (Universita di Padova)

Very recently, a series of papers dealing with the reduction of organic halides at silver cathodes have appeared.[1] 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. 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. 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.

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.

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 $\upsilon = 0.2$ Vs^{-1}.

Compound	GC	Hg	Ag	
	E_p[a]	E_p[a]	E_p[a]	E_p (CO_2)[a,b]
CO_2	-2.41	-2.46	-2.34	
$PhCH_2Cl$	-2.25	-2.27	-1.79	-1.52
4-CF_3-$PhCH_2Cl$	-1.99	-1.97	-1.67	-1.48
4-CH_3O-$PhCH_2Cl$	-2.26	-2.31	-1.82	-1.52
$PhCH(CH_3)Cl$	-2.23	-2.29	-1.81	-1.53

[a] In V vs. SCE. [b] In the presence of 0.28 M CO_2.

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. Instead, the E_p values obtained at Ag are considerably less negative than those measured at GC. Such a great difference of E_p between the two electrodes points to a significant electrocatalytic effect of the silver electrode towards the reduction of RCl.

The most relevant outcome of the voltammetric investigation is that, at Ag cathodes, reduction of RCl occurs at potentials considerably less negative than E_p of CO_2. In the least favorable 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.

Table 2 Electrocarboxylation of benzyl chlorides in CO_2-saturated CH_3CN + 0.1 M ET_4NClO_4.

Entry	RCl	Cathode	E_{app}[a]	n[b]	Product yields[c]	
					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-CF_3-$PhCH_2Cl$	Ag	-1.55	2.32	2	95
7	4-CH_3O-$PhCH_2Cl$	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^-/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.

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.[2] 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,[3] 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 less negative than, those of the most efficient catalysts so far reported[4] 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.

References

1. (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.
2. An exception is when the experiment was conducted in a divided cell (entry 2). In that case, only a moderate yield of phenyl acetic acid was obtained together with $PhCH_2CO_2CH_2Ph$ arising from esterification of the carboxylate with $PhCH_2Cl$. This outcome underlines the importance of the sacrificial consumable anode methodology in electrocarboxylation of organic halides.
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4. A. Gennaro, A. A. Isse and F. Maran, *J. Electroanal Chem.*, 2001, **507**, 124 and the references cited therein.