Electrochemical Reduction and Carboxylation of Chloroacetonitrile

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The electrochemical reduction of organic halides has been extensively investigated as an example of dissociative Electron Transfer (ET) with carbon halogen bond fragmentation.[1] Furthermore in CO_2-saturated aprotic solvents carboxylic acids were obtained, with high faradic and chemical yields, when electrolyses were performed in undivided cells with sacrificial Al or Mg anodes.[2]

Cyanoacetic acid and its derivatives such as alkyl cyanoacetates are employed as starting materials in many industrial processes. The current method of production of this acid makes use of the reaction between chloroacetic acid and alkali metal cyanides.[3] Alternative methods of synthesis, involving less dangerous reagents, have been described in a number of patents.[4,5]

In this paper we describe results on the electrochemical reduction of chloroacetonitrile in aprotic solvents in the presence of CO_2 at two different electrode materials and in different cell arrangements.

At a Hg or glassy carbon (GC) electrode, chloroacetonitrile gives rise to a single irreversible, broad peak in either DMF or MeCN. At both electrodes, E_p varies linearly with $\log \upsilon$, the average of the slope $\partial E_p / \partial \log \upsilon$, measured in both solvents, being 96 mV/decade at Hg and 94 mV/decade GC. Also the peak width $\Delta E_{p/2}$ was measured in both solvents by using both electrodes. The values obtained at $\upsilon = 0.2$ Vs^{-1} lie in the range 140-170 mV. These results are typical of the electrode reduction of alkyl halides, which undergo dissociative ET to yield $R^\bullet$ and X^-. The reduction potential of $NCCH_2^\bullet$ in DMF is more than 1.0 V less negative than E_p of $NCCH_2Cl$. The process underlying the irreversible peak is thus

$$NCCH_2Cl + e^- \longrightarrow NCCH_2^\bullet + Cl^- \qquad [1]$$

$$NCCH_2^\bullet + e^- \rightleftarrows NCCH_2^- \qquad [2]$$

Reaction 1 may occur in a single step, C–Cl bond rupture being concerted with ET, or in two separate steps with intermediate formation of a radical anion. Convolution analysis of voltammetric curves obtained at GC in DMF leads to the conclusion that the ET to chloroacetonitrile is more likely to occur via a step-wise mechanism.

The carbanion $NCCH_2^-$ formed in Eq. 2 reacts with the starting halide which acts as proton donor. When CO_2 is bubbled into a DMF or MeCN solution of the chloride a remarkable increase of the peak current is observed. In the presence of CO_2, nucleophilic attack of $NCCH_2^-$ on CO_2 (Eq. 3) outruns the father-son reaction leading to an increase of the peak current. In these conditions reduction of the chloride tends to become a 2e$^-$ process.

$$NCCH_2^- + CO_2 \longrightarrow NCCH_2CO_2^- \qquad [3]$$

The results of preparative scale electrolyses of chloroacetonitrile in DMF and MeCN, in the presence of CO_2, are reported in Table I. The electrolyses were performed using two different cells: a two compartment cell with a Pt anode separated from the cathodic compartment by a medium porosity glass frit or an undivided cell with a sacrificial Al anode. Both Hg and graphite (C) cathodes were employed. The main reduction products obtained in both cases were cyanoacetic acid (RCO_2H) and acetonitrile, while succinonitrile was either absent or observed at trace levels.

In MeCN the electrolyses in the divided cell give satisfactory RCO_2H yields (60–61%) at either electrode. When an undivided cell is used, excellent acid yields reaching 93% are obtained. A comparison between the results reported in the Table shows that better results in terms of acid yield are obtained in MeCN than in DMF. The higher concentration of CO_2 in MeCN as compared to DMF[6] may be, at least in part, responsible for the observed increase of cyanoacetic yield on passing from DMF to MeCN.

Table I. Electrochemical carboxylation of chloroacetonitrile in DMF or MeCN + 0.1 M TBAP

Solv.	Cell[a]	El.	[RCl] mM	E^b V	n^c	RH (%)[d]	RCO_2H (%)[d]
DMF	A	Hg	47.5	-1.75	1.6	21	41
DMF	A	C	47.5	-2.05	2.0	9	30
DMF	B	Hg	47.5	-1.75	2.2	8	47
DMF	B	C	47.5	-2.05	2.2	9	73
MeCN	A	Hg	47.5	-1.75	1.9		61
MeCN	A	C	50.7	-1.95	2.2		60
MeCN	B	Hg	50.7	-1.67	2.3		93
MeCN	B	C	49.9	-1.95	2.3		91

[a] The cell used for electrolysis was either a two compartment cell (A) or an undivided cell with aluminum sacrificial anode (B). [b] Electrolysis potential (vs. SCE). [c] Charge (F/mol) consumed with respect to converted $NCCH_2Cl$. [d] Yield is calculated with respect to $NCCH_2Cl$ disappeared.

References

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