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Organic electrosynthesis with a sacrificial anode. Chemical reductive degradation of the solvent N,N-dimethyl formamide

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When electrolyses using a sacrificial magnesium anode are carried out in DMF as solvent, an overconsumption of the metal is observed (10 to 60%) which principally depends on the temperature and the current density. It has been shown that the electrochemical scouring of magnesium induces a chemical reduction of DMF and a possible pathway is proposed.

1. Introduction

The poor efficiency of ion exchange membranes in organic media (selectivity, durability, high ohmic drop, . . .) stands in the way of the growth of organic electroreductive syntheses in divided cells. The use of sacrificial anodes, which has increased in recent years, may help to overcome this drawback. Indeed, various electroreductions, generally involving carbon–carbon bond formation, have been successfully performed in this way with undivided cells.

The most recent synthetic applications have been devoted to the electroreductive coupling of organic halides (RX) with various electrophilic reagents. The metal (M) of the sacrificial anode is an easily oxidizable one such as magnesium, aluminium or zinc. The electrochemical balances are expressed as

$$\mathrm{M} \longrightarrow \mathrm{M}^{n+} + ne \qquad \text{(for the anode)} \quad (1)$$

$$\mathrm{RX} + 2\mathrm{e} \longrightarrow \mathrm{X}^- + \mathrm{R}^- \xrightarrow{\text{electrophile}} \text{products} \qquad \text{(for the cathode)} \quad (2)$$

Though the point is not yet clearly understood, the ions generated by the metallic anode are often involved in the cathodic process to ensure the desired reaction.

In this way, from carbon dioxide, carbonyl compounds or anhydrides as electrophiles, carboxylic acids [1–3], alcohols [4] and ketones [5] are obtained, respectively. Of these reactions, the electrosynthesis of carboxylic acids is the most advanced since an industrial unit providing a production of 50 kg per day is now operating [6].

The method is efficient with various organic halides (benzylic, aromatic, . . .) dissolved in N,N-dimethylformamide (DMF) (10 to 20% w/w). The cathode consists of stainless steel and the anode of magnesium. Electrolyses are performed at near ambient temperature under a low pressure of carbon dioxide, by setting a constant current density in the range 200 to 600 $\mathrm{A\,m^{-2}}$ [7]. The organic halide is then converted with good yields into a carboxylate ion, according to the overall reaction

$$\mathrm{RX} + \mathrm{CO_2} + \mathrm{Mg} \longrightarrow \mathrm{RCO_2^-} + \mathrm{Mg^{2+}} + \mathrm{X^-} \quad (3)$$

This balance is equivalent to that obtained via a classical Grignard reaction. Nevertheless, the electrolytic process involves only one step, thus avoiding the hazardous preparation of the organometallic intermediate from divided magnesium in ethereal solvents. During the investigation of the scope and limitations of the process, as well as its scale up, some difficulties have been encountered which can be summarized as follows.

We have shown that the consumption of magnesium is always higher than that expected from a two-electron oxidation. If we assume that only divalent magnesium can be generated by the electrooxidation, it becomes evident that a chemical oxidation of the metal occurs. Therefore, we have decided to search for evidence concerning the nature of the oxidizing species involved and the influence of experimental conditions on this chemical corrosion. We have also tried to examine to what extent this side reaction may be correlated with the drastic passivation of the cathode which is observed in some cases, thus inducing a high cell-voltage and a big decrease of the faradaic yield of the reduction of the organic halide.

2. Experimental details

2.1. *Overconsumption of magnesium*

Figure 1 represents the undivided cell used for the electrosyntheses of carboxylates in solvent DMF, and the measurement in these conditions of the consumption of magnesium. The cathode was a cylindric stainless steel grill (20 $\mathrm{cm^2}$). The anode was a rod of

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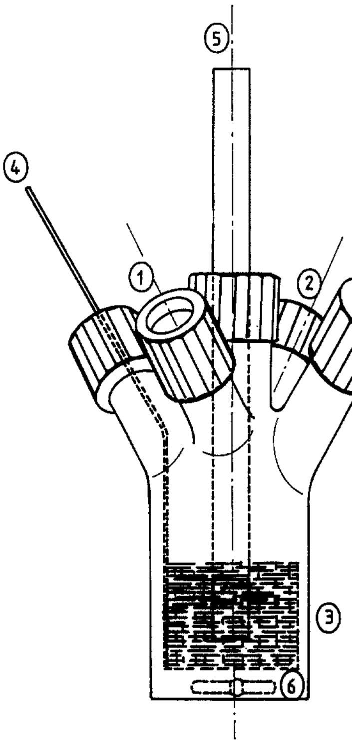


Fig. 1. Electrochemical undivided cell: (1) and (2) Input and output of CO_2; (3) Stainless steel grid; (4) Electrical connection; (5) Magnesium rod; (6) Magnetic stirrer.

magnesium (purity 99.8 %, diameter 1 cm). This rod was cleaned with dilute HCl, rinsed then dried before use. The upper part of the rod was sheathed with a silicon tube to control the immersed area accurately (1.2 to 6.3 cm^2).

The solvent DMF was distilled over anhydrous copper sulphate and under a reduced pressure just before use. The supporting electrolytes Bu_4NBr, Bu_4NBF_4 were stored in a vacuum dessicator. Other reagents were of commercial grade.

During electrolyses the cell was immersed in a thermostated bath and the solution was stirred magnetically.

The magnesium consumption was measured by weighing the rod before and after electrolysis. The faradic yield (R_f) of the anodic reaction was then expressed as

$$R_f = \frac{2 \times 96\,500 \times \Delta m}{24.3 \times C} \qquad (4)$$

where Δm is the loss of mass (g) of magnesium and C the charge (Coulomb).

2.2. *Degradation of the solvent*

Experiments were carried out in a two-compartment cell separated by a sintered glass disk. When pyridine was the solvent it was distilled over potassium hydroxide just before use. The cathodic reaction was the reduction, on a platinum gauze, of the easily reducible 1,2-dibromoethane, which was then converted into ethylene. The anolyte was fitted with a magnesium rod (6.3 cm^2). Supporting electrolytes were added (0.3 M) to ensure good ionic conductivity. Nevertheless, only a low current (60 mA) was set owing to the significant ohmic drop induced by the separator.

Gas chromatography (GC) with various columns and appropriate internal standards was used for the determination of organic compounds. Evidence was sought for the degradation of DMF when used as the solvent, by treating samples of the anodic solutions in the following manner.

2.2.1. Reducing properties. The first method was the addition of iodine in excess, acidification and back titration by sodium thiosulphate. (Average value: 0.7 to 0.9 electron-mol/mol of overconsumed Mg).

The second method was the addition of aliquots of a solution of 2,2-diphenyl-1-picryl-hydrazylhydrate (DPPH) and following of the ultraviolet spectra [8] (average value 1.1 to 1.3 electron-mol/mol of overconsumed Mg).

2.2.2. Basic properties. The anolyte was treated with aqueous HCl. The back titration of the excess strong acidity indicates that 3.3 mol of basic species were obtained per mole of overconsumed Mg.

2.2.3. Nucleophilic properties. Acid anhydrides (acetic, propionic or butyric) were added (0.5 M) and solutions were allowed to react overnight. The N,N-dimethylamides obtained were identified by chromatography on a capillary column coupled with a mass spectrometer. GC indicated the formation of 0.4 to 0.6 mol of amide per mole of overconsumed Mg.

If anhydrides were added before electrolyses, amides were also obtained, but in lower amounts. At the same time the anodic faradaic yield was increased. As previously described [9], anhydrides may react with anodized magnesium and then compete with DMF. Results are not reliable in such conditions.

2.2.4. Identification of glyoxal. A first method was the reaction with 2-aminothiophenol and ultraviolet analysis [10].

A second method was the addition of an acidic solution (water/ethyl alcohol) of 2,4-dinitrophenylhydrazine, filtration, washing and drying of the orange precipitate obtained. The formation of the *bis*-hydrazone adduct of glyoxal was checked by control of the melting point (obtained 333° C; 328° C [11]). Gravimetry indicated, approximately, the recovery of 0.5 mol of glyoxal per mole of overconsumed Mg.

All these experiments, intended to provide evidence for the degradation of the solvent, were compared with 'blank solutions' of DMF containing the same reagents including divalent magnesium ions arising from available magnesium halides.

3. Results and discussion

3.1. *Overconsumption of the magnesium anode*

Initial experiments, intended to observe the influence of various parameters on the faradaic yield of the

Table 1. Overconsumption of the magnesium anode

Run	*Organic halide*	*Conc.* (*M*)	*Temp.* (°*C*)	*Charge* (*C*)	R_f
1	1,2-Dichlorobenzene	0.53	35	1500	1.44
2	Chlorobenzene	0.6	35	1500	1.40
3	Benzylchloride	0.52	35	1500	1.49
4	4-Chloroanisole	0.5	35	1500	1.46
5	3-phenoxy(α-methyl)-benzyl chloride	0.61	35	1500	1.55
6	4-Chloro-trifluoromethyl-benzene	0.6	35	1500	1.46
7		0.3	35	1500	1.50
8		1.2	35	1500	1.48
9		0.6	35	500	1.50
10		0.6	35	3000	1.48
11		0.6	5	1500	1.17
12		0.6	15	1500	1.19
13		0.6	25	1500	1.49
14		0.6	75	1500	1.49

General conditions: DMF 25 ml + Bu_4NBr 5 × 10^{-2} M; set intensity = 0.3A; magnesium area = 6.3 cm^2; CO_2 bubbling at atmospheric pressure.

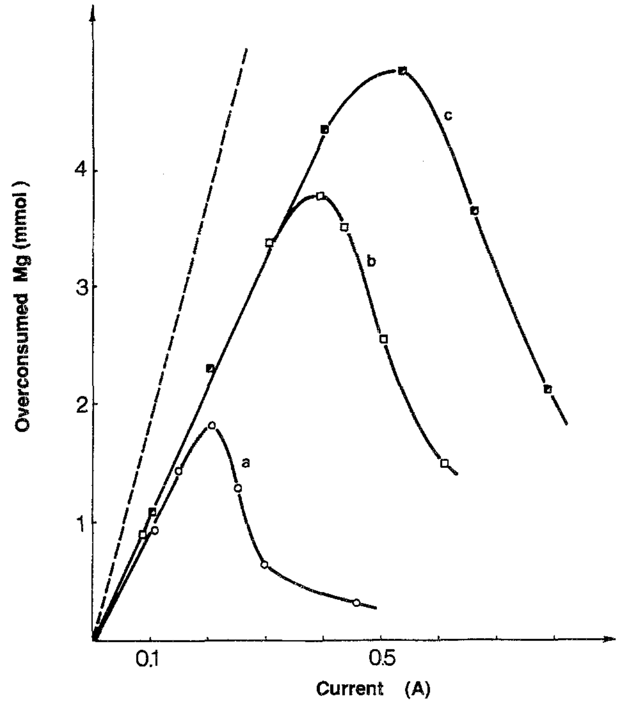


Fig. 2. Overconsumption of the magnesium anode as a function of the set current. General conditions: DMF + Bu_4NBr (5 × 10^{-2} M) + 4-CF_3-C_6H_4Cl (0.8 M) CO_2 (1 atm); T = 35° C. Time of electrolysis, 1 hour. Electrode areas: (a) 1.2 cm^2 (○), (b) 3.5 cm^2 (□), (c) 6.3 cm^2 (◪). Dotted line corresponds to the electrochemical consumption.

magnesium oxidation, were carried out in conditions similar to those used for electrosynthesis of carboxylates.

The results presented in Table 1 show that the overconsumption of magnesium does not significantly depend on either the nature or the concentration of the tested halides (runs 1 to 8), or the extent of the electrolytic reaction (runs 6, 9, 10). On the other hand, the results obtained from runs 6 and 11 to 14 clearly indicate that an accelerated corrosion with increasing temperature is superimposed upon the electrodissolution.

Since the observed values of the faradaic yield (R_f) are always greater than 1, the rate (V_c) of this chemical corrosion may be calculated according to

$$\frac{n_e + n_c}{n_e} = R_f \tag{5}$$

$$V_c = \frac{dn_c}{dt} = (R_f - 1)\frac{dn_e}{dt} = \frac{(R_f - 1)\, I_{(A)}}{2 \times 96\,500} \tag{6}$$

where n_e and n_c are the moles of magnesium consumed electrochemically and chemically, respectively.

As shown in Fig. 2, R_f and then V_c crucially depend on the current (I) or, more precisely, on the current density. For this set of experiments, the duration of the electrolysis was the same and the temperature was kept at 35° C. We show that, at low current densities, V_c rises proportionally with the intensity (R_f # constant = 1.5). We suppose that, by increasing I, the electrolysis induces a more and more efficient scouring of the magnesium surface. In all cases the chemical corrosion was stopped when the current was switched off. The decrease in V_c further observed at high current densities may be explained by the more anodic polarization of the metal, consequently attenuating its reducing power.

Such a behaviour of magnesium has been mentioned previously [9]. The authors have effectively shown that anodic polarization can promote the reduction by the metal of various organic compounds such as acids, acid halides, esters, carbonyl derivatives, etc. Therefore we have tried to identify, in our experimental conditions, the nature of the reagents and the products involved in this chemical oxidation of magnesium.

3.2. *Degradation of the solvent DMF*

Experiments were carried out in a two-compartment cell to eliminate reductions induced by cathodic processes.

Firstly, DMF was used as the solvent. The anodic compartment was fitted with a magnesium rod and electrolyses were performed at 30° C with a constant current of 60 mA. Whatever the electrolyte used (Bu_4NBr, Bu_4NBF_4 or LiCl) and the extent of the electrolyses, the values of R_f stayed in the range of 1.44 to 1.49. The presence of carbon dioxide and 4-chlorotrifluoromethylbenzene had no influence and the aromatic halide was not consumed. On the other hand part of the DMF has undergone a degradation, as proved by analysis of the solution (see experimental section).

Secondly, DMF was used as a solute in pyridine (+ Bu_4NBr, 0.3 M) since Rausch *et al.* [12] have shown that no overconsumption of magnesium was observed by electrooxidation in this solvent. On account of the weak solubility of magnesium salts in pyridine [13] the temperature was set at 60° C. In these conditions, R_f exceeded the theoretical value only when DMF was added to the anolyte and the amide was partially consumed. Once again the addition of an aromatic halide had no effect. These results, collected in

Table 2. Reaction of DMF with anodized magnesium in pyridine

Amount DMF (m mol)	*Charge (C)*	R_f	*Magnesium overconsumed (m mol)*	*DMF* consumed (m mol)*
0	500	1.01	0	–
2.44	390	1.19	0.38	
10.50	640	1.37	1.25	2.39
12.00	535	1.37	1.0	1.8
13.25†	870	1.59	2.65	5.2

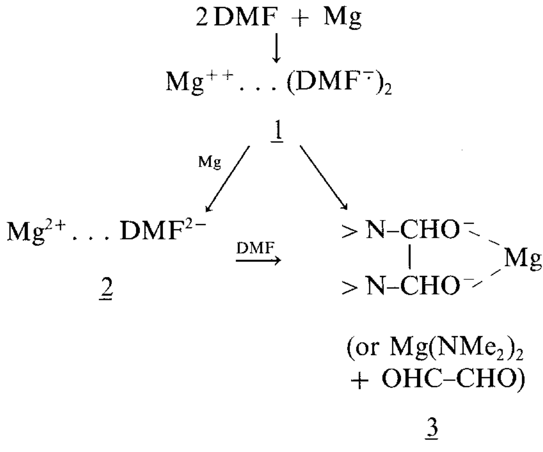
General conditions for anolyte: 25 ml Pyridine + 3 g Bu_4NBr; I = 60 mA; T = 60° C; inert atmosphere (argon).
* Determination by gas chromatography.
† 0.5 M pCF_3-C_6H_4Cl was added.

Table 3. Electrooxidation of sacrificial anodes in various solvents

Solvent	*Anode*	R_f
N,N-Dimethylformamide	Mg	1.5
N,N-Dimethylformamide	Al	1.1
N,N-Dimethylformamide	Zn	1.0
Pyridine	Mg	1.0
Pyridine	Al	1.1
N,N-Dimethylacetamide	Mg	1.5
N,N-Dibutylformamide	Mg	1.1
N-Methylpyrrolidone	Mg	1.05

General conditions: Divided cell, 0.3 M Bu_4NBr; anode area 6.3 cm²; I = 0.3 A; T = 35° C (except in pyridine 60° C); time of electrolysis, 1 hour.

Table 2, clearly indicate that the chemical corrosion of magnesium is mainly induced by DMF and agrees with a stoichiometry involving two moles of DMF per mole of magnesium. In accordance with previous work [8] related to the reduction of DMF, either electrochemically or by means of sodium, we assume the following scheme as a possible pathway



(7)

The formation of amides when anhydrides are added to the electrolytic solution may be interpreted by a reaction with 3 which can give rise to $(CH_3)_2N^-$ anions. By analogy, it can be assumed that when electrolyses are achieved under carbon dioxide pressure 3 may yield magnesium dimethylcarbamate. Attempts to identify this product were unsuccessful. In the same way the reaction of 3 with protons may then lead to glyoxal and dimethylammonium cations. The theoretical balance involves 4 mol H^+ per mole of overconsumed magnesium. We have found a value of 3.3. Furthermore, we have given evidence for the formation of glyoxal.

Such a reductive degradation of the DMF has also been observed in the preparative experiments, that is, in an undivided cell and in the presence of the reagents (RX and CO_2). However, in these conditions we cannot discriminate the chemical anodic reaction and the possible alternative cathodic process.

3.3. *Behaviour of various solvents and anodes*

Results in Table 3 show that the chemical corrosion of anodized magnesium depends largely on the nature of the tested solvents. For instance, behaviour quite similar to that of DMF is obtained from N,N-dimethylacetamide. In the same way, after electrooxidation of a magnesium rod in this solvent, the addition of butyric anhydride to the resulting anolyte leads to N,N-dimethylbutyramide (0.6 mol/mol of overconsumed Mg). We have also given evidence for the formation of butanedione by hydrolysis of the solution.

We have tested zinc and aluminium which are also valuable sacrificial anodes for electrosyntheses [1, 2, 4, 5]. The faradaic oxidation yield is scarcely higher than the theoretical value, indicating that a chemical corrosion of these metals by the solvent DMF is weak or absent.

4. Conclusion

The aim of this work was to explain the cause of the magnesium overconsumption observed when this metal is used as a sacrificial anode for electrocarboxylation of organic halides. It has been clearly shown that the chemical corrosion mainly involves a reductive degradation of the solvent and a plausible mechanism has been advanced. We assume that resulting products, such as weakly soluble magnesium salts, are responsible for the cathodic passsivity which sometimes occurs in the course of exhaustive electrolyses. Although some experimental observations agree with this assumption it is still to be clarified and work is in progress to check whether insulating layers are formed which may involve either degradation products of DMF or other compounds.

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