JOURNAL OF APPLIED ELECTROCHEMISTRY 12 (1982) 549–555

Electrochemical carboxylation of organic substrates. Synthesis of carboxylic derivatives of acenaphthylene

S. GAMBINO, G. FILARDO, G. SILVESTRI

Istituto di Ingegneria Chimica, Facoltà di Ingegneria, Viale delle Scienze, Palermo, Italy

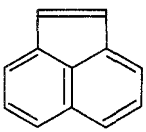
Received 23rd December 1981

The electrochemical carboxylation of acenaphthylene to *trans*-acenaphthene-1,2-dicarboxylic acid and acenaphthene-1-carboxylic acid has been investigated. The yields of the synthesis are influenced by the cathode material by the current density and, in the case of acenaphthene-1-carboxylic acid, by the pressure of carbon dioxide. In preparative experiments, performed in a 'gas lift' electrochemical cell, up to 100 g of *trans*-acenaphthene-1,2-dicarboxylic acid were obtained at cathodic current densities of 40 mA cm^{-2} and with current yields greater than or equal to 80%.

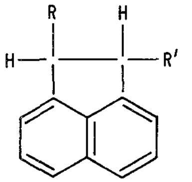
1. Introduction

The electrochemical production of carboxylic acids by insertion of carbon dioxide has been the object of several studies in the past. In fact, a great number of compounds of potential interest can be prepared following that procedure, e.g. monocarboxylic acids starting from various derivatives such as halides [1], carbonyl compounds [2] or alkenes [3]; and dicarboxylic acids, starting from various unsaturated compounds [4]. Generally however, these reactions have been studied on a small laboratory scale, and no particular attention has been paid to the problems raised by the performance of large-scale preparative electrolyses. As far as the authors know, these problems have been faced only in the case of the self carboxylation of carbon dioxide to oxalate anions [5].

Our research group has been involved in the study of synthetic processes involving carbon dioxide [6]. During the development of this study, we chose the insertion of carbon dioxide into acenaphthylene(I) leading to mono or dicarboxylic derivatives of acenaphthene(II) as a model reaction.



I



II

R = COOH
R' = H, COOH

The essential features of many carboxylations, already quoted in the literature, are the same as those found for acenaphthylene. The substrate is highly soluble in electrolytic media, several inorganic salts of the dicarboxylic acid have a low solubility, and, moreover, the yields and selectivity of the synthesis on the bench-scale are fairly good.

It is known from the literature that the reduction of acenaphthylene with alkaline or alkaline earth metals in the presence of carbon dioxide gives very poor yields of acenaphthene-1-carboxylic acid (20%) and good yield of *trans*-acenaphthene-1,2-dicarboxylic acid (90%) but the conversion of acenaphthylene does not exceed 50%, and the experimental procedure appears rather complicated [7]. Moreover, these reactions do not show a high selectivity towards the 1,2 positions of acenaphthylene: acenaphthene-1,3-dicarboxylic and acenaphthene-1,5-dicarboxylic acids are obtained as byproducts.

The electrochemical process we have studied offers a simplified procedure for the synthesis of both acids, and gives, depending on the composition of the electrolytic medium, good yields either of the mono or dicarboxylic acid.

2. Experimetal procedure

2.1. *Small-scale experiments*

Commercial *N,N*-dimethylformamide was distilled at 20 mm Hg and dried over 4A molecular sieves

0021–891X/82/050549–07$03.34/0

just before each experiment. Acenaphthylene and the tetraalkylammonium salts were crystallized from ethyl acetate and dried under vacuum until a constant melting point was reached. The usual electrochemical apparatus was employed in the syntheses. Cyclic voltammograms were recorded with a potentiostat, AMEL 552, equipped with a function generator, AMEL 567. The reference electrode was Ag/AgI in 0.1 mol dm^{-3} Bu_4NI in DMF.

2.1.1. Trans-*acenaphthene-1,2-dicarboxylic acid.* The electrolyte, DMF (70 cm^3), Bu_4NBr (0.1 mol dm^{-3}), acenaphthene (3–5 g), was placed in a diaphragmless cell arranged with an efficient magnetic stirring and a glass frit gas bubbler. Cylindrical electrode symmetry was employed in all the experiments (external cathode with 100 cm^2, and internal anode with 15 cm^2 apparent surfaces). When a mercury pool cathode was used, an aluminium disc anode was placed, parallel to the cathodic surface, at a distance of about 15 mm. The electrolyte was saturated with carbon dioxide by bubbling continuously throughout the electrolysis. Cathodic current densities of 1.9–5.3 mA cm^{-2} were used. The conversion of acenaphthylene to the corresponding acid was followed by periodic U.V. spectroscopy of samples extracted from the electrolyte (the adsorption peaks were at 323 nm for acenaphthylene and at 293 nm for the dicarboxylic acid). Sacrificial aluminium or zinc anodes were employed and during the electrolysis, the precipitation of the corresponding salt of the acid occurs. At the end of the electrolysis the solvent was distilled off at a reduced pressure. The yellow powder recovered was hydrolysed with 0.1 mol dm^{-3} HCl at room temperature for 2 h. The pale yellow acid was filtered and crystallized from benzene–acetic acid. Product yields ranging from 68 to 85%, with current efficiencies of 70 to 80% were obtained.

2.1.2. *Acenaphthene-1-carboxylic acid.* The synthesis is the same as that described for the dicarboxylic acid. The initial composition of the electrolyte was modified by addition of acetic acid (0.5–1.2 vol%). Product yields ranged from 35 to 60%, the main by-products being the dicarboxylic derivative and acenaphthene at lower and at higher acid concentrations, respectively.

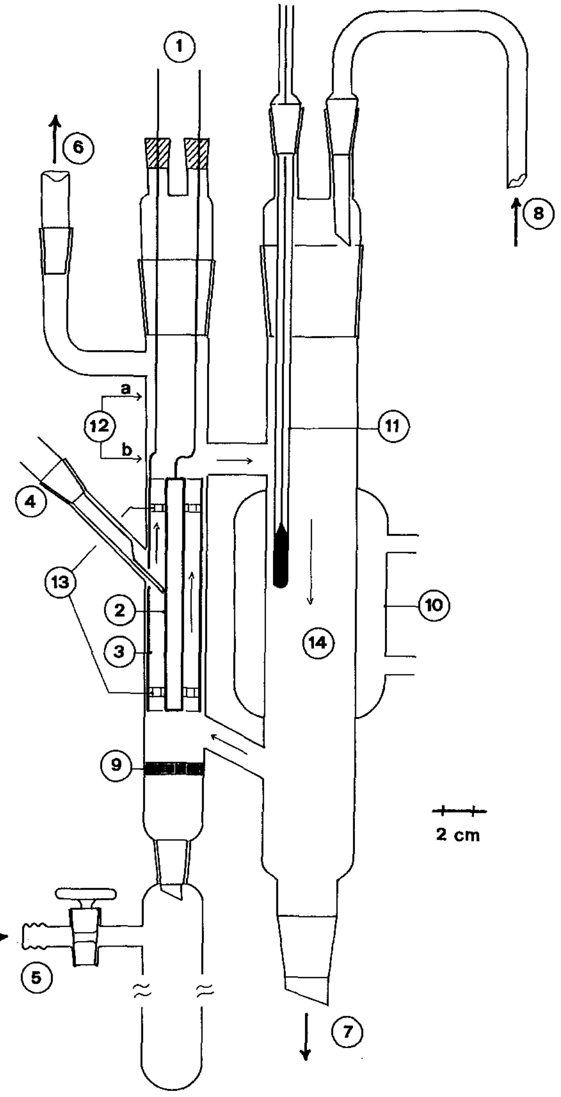


Fig. 1. Gas lift electrochemical cell. 1. electrical connections; 2–3. cyclindric electrode system; 4. reference electrode; 5. carbon dioxide inlet; 6. carbon dioxide outlet; 7. solution exit to the filter; 8. recycling of the solution after the filtration; 9. porous glass frit grade 3; 10. water refrigerator; 11. thermometer; 12. maximum (a) and minimum (b) levels of the the electrolytic solution during the electrolysis; 13. spacers; 14. reservoir.

2.2. *Large-scale electrolysis*

The preparative experiments were performed in the electrolytic cell shown in Fig. 1. The cell design is analogous to the so-called 'gas lift cells' [8]. The electrolyte is forced to circulate from the reservoir (14) to the electrode system (2–3) by the buoyancy forces generated by the bubbling

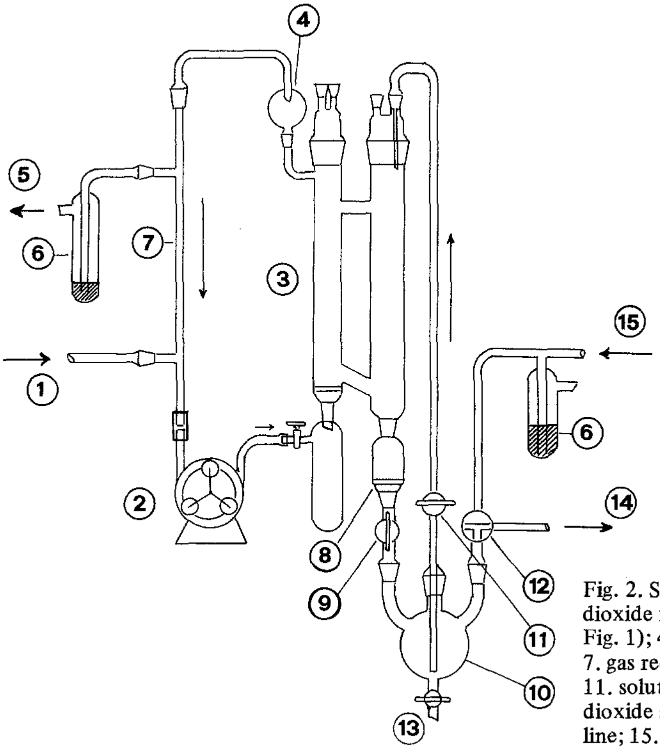


Fig. 2. Scheme of the electrolysis system. 1. carbon dioxide feed; 2. peristaltic pump; 3. electrolysis cell (see Fig. 1); 4. foam breaker; 5. purge; 6. mercury valve; 7. gas recycle; 8. filter; 9. filter valve; 10. solution holder; 11. solution recycle valve; 12. vacuum-pressurized carbon dioxide switch; 13. solution discharge valve; 14. vacuum line; 15. pressurized carbon dioxide line.

of carbon dioxide through the frit (9). The electrolyte fills the cell from the minimum to the maximum levels (12a, b). The electrode system has cylindrical symmetry, with aluminium or zinc anodes. The aluminium or zinc salts of the dicarboxylic acid are poorly soluble in DMF and were progressively filtered off through the connection (7) to a filter. The mother liquor was recycled through (8).

The whole system including the electrolytic cell is shown in Fig. 2. Carbon dioxide was fed from (1) to a recycle loop (7), forced by the peristaltic pump (2) to the cell (3) and recycled. The pressure of the system was regulated by the level of mercury in the valve placed at the purge (5). In our experiments the internal pressure of the cell corresponded to a mercury height of about 10 mm. The precipitate formed during the electrolysis was collected by a filter at (8). The filtration and the following recycling of the solution was repeated several times during the electrolysis. At each cycle the level of the solution was maintained between the maximum and minimum levels (12) shown in Fig. 1. The zinc salt was filtered quite easily whereas the aluminium salt was separated best by centrifuging as the microcrystalline slurry easily blocked the filter. No moving parts were in contact with the solution: the filtration and the recycling to the cell were carried out by switching (12) to the vacuum line (14) or to the pressurized CO_2 line (15). The determinations of the current yields reported in this paper were made by limiting the conversion of acenaphthylene to 25% of the initial charge.

Long-range preparative experiments at fairly constant acenaphthylene concentration were performed using a five-necked flask as holder (10). The concentrated solution was passed in through the fifth neck, and the spent solution was discharged through valve (13). After a period depending on the crystal size of the precipitate, the filter (8) must be replaced, recovering the salt obtained (10–35 g per cycle): the solution was discharged through a valve (13) and the filter (8) disconnected. The salt was washed with acetone, then dried under vacuum and hydrolysed with 10% HCl at room temperature for 10 h. The carboxylic acid was filtered, dried and crystallized from 9 : 1 benzene–acetic acid (see experiment 1, Table 4).

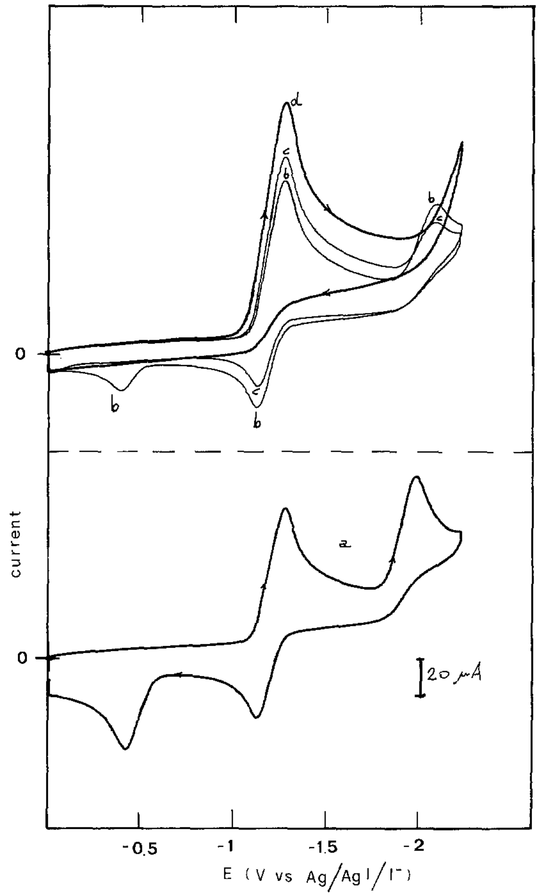


Fig. 3. Cyclic voltammograms at vitreous graphite of 10^{-2} mol dm^{-3} acenaphthylene in DMF–Bu_4NBr (0.1 mol dm^{-3}). (a) acenaphthylene alone; (b, c and d) acenaphthylene at increasing CO_2 concentration; cathode area 3 mm^2; scan rate 100 mV s^{-1}; reference electrode Ag/AgI/I$^-$ 0.1 mol dm^{-3} in DMF.

3. Results

3.1. *Electroanalytical determinations.*

The electroanalytical behaviour of acenaphthylene does not differ qualitatively from that of many aromatic polynuclear compounds: the cyclic voltammogram at vitreous graphite shows two reduction peaks at − 1.28 and − 1.98 V (see curve a in Fig. 3). The presence of carbon dioxide modifies the pattern, giving just one irreversible reduction peak corresponding to a two electron step (curves b–d). No catalytic charge transfer was observed for acenaphthylene and CO_2.

The same behaviour is observed when proton donors such as acetic acid are added to the solution.

Table 1. The dicarboxylation of acemaphthylene as a function of the pressure of carbon dioxide

Experiment	*CO_2 pressure* (atm)	*Cathodic current density* (mA cm^{-2})	*Product yield* (%)	*Current yield* (%)
1	17.2	1.9	81	75
2	5.7	1.9	79	75
3	1.1	1.9	76	74
4	15.3	5.3	74	71
5	5.9	5.3	73	72
6	1.1	5.3	69	70

Cathode: porous graphite; anode: aluminium;
2 g acenaphthylene; 65 cm^3 DMF–Bu_4NBr (1.0 mol dm^{-3}); $T = 20°$ C.

3.2. *Small-scale synthetic experiments.*

Depending on the composition of the electrolyte, and on the electrolysis conditions, variable quantities of high molecular weight products, derived from the oligomerization of acenaphthylene, are formed.

Concentrations of carbon dioxide higher than the saturation value at atmospheric pressure have only a minor influence on the yields in the dicarboxylation process (see Table 1). No significant differences were noticed when the pressure was raised to 18 atm. The cathode material has a significant influence on the yields: the best results were obtained with graphite, copper, zinc and mercury; aluminium and stainless steel gave poor results (see Table 2).

In the presence of proton donors, it is possible to perform the monocarboxylation process, but the side reactions, the hydrogenation to acenaphthene and hydrogen evolution also occur. The competitive reactions of monocarboxylation and hydrogenation can be directed by proper adjustment of the [HX]/[CO_2] molar ratio. In fact, at high acid concentrations, good yields of the monocarboxylic acid derivative are obtained performing the electrolysis under moderate pressures of carbon dioxide (see Table 3). In the range of synthetic conditions studied so far, no oxalic acid has been found among the products even at higher carbon dioxide concentrations.

Water concentrations up to 0.1% do not modify the yields of the monocarboxylation or the

Table 2. The carboxylation of acenaphthylene with different cathode materials

Experiment	*Cathode*	*Acenaphthylene* (g)	*Charge passed* ($\times 10^{-2}$ F)	*Product yield* (%)	*Current yield* (%)
1	Stainless steel AISI 320	2.5	4.22	52	40.5
2	Graphite	2.0	2.9	72	65
3	Aluminium	2.4	4.3	30	22
4	Mercury	2.3	3.27	65	61.4
5	Zinc	2.8	3.9	80	78.5

Cathodic current density, 3 mA $\mathrm{cm^{-2}}$; anode, aluminium; 65 $\mathrm{cm^3}$ DMF–$\mathrm{Bu_4NBr}$ (0.1 mol $\mathrm{dm^{-3}}$); $T = 20°$ C.

Table 3. Electrochemical synthesis of acenaphthene-1-carboxylic acid

Experiment	*CO_2 pressure* (atm)	*Acetic acid* (vol %)	$[\mathrm{CO_2}]/[\mathrm{HX}]$	*Product yields (%)*		
				Monocarboxylic acid	*Dicarboxylic acid*	*Acenaphthene*
1	6	1	9.2	67	9.2	–
2	1.1	1	1.5	40	–	45
3	1.1	4	0.38	60	–	35
4	1.1	10	0.15	27	–	48

Anode, aluminium; cathode, graphite; 65 $\mathrm{cm^3}$ DMF–$\mathrm{Bu_4NBr}$ (0.1 mol $\mathrm{dm^{-3}}$); $T = 20°$ C.

dicarboxylation. This result is apparently in contrast to those obtained by other authors [4], and can be explained on the basis of the water sequestering action of the cationic species $\mathrm{Al^{3+}}$ or $\mathrm{Zn^{2+}}$ which originate at the sacrificial anode.

3.3. *Preparative experiments*

Using the preparative system shown in Fig. 2, the dependence of the behaviour of the system on the acenaphthylene concentration, on the flow rate of the solution and on the cathodic current density, was studied. The flow rate of the electrolyte in the annular electrolytic system was regulated by the flow rate of carbon dioxide through the cell. The polarization curves at different concentrations of acenaphthylene were determined at flow rates of the electrolyte of 0, 0.6, 1.3, 1.8 $\mathrm{dm^3\,min^{-1}}$ (see Fig. 4)*. As expected, the influence of the flow rate of the solution on the slope of the polarization curve becomes less at

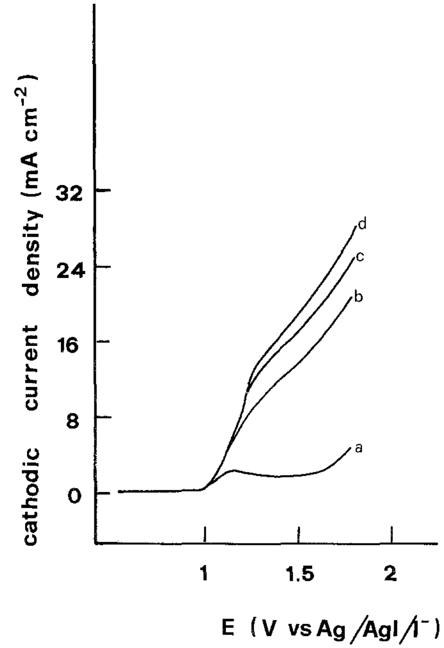


Fig. 4. Current–voltage curves at different flow rates of the electrolyte: (a) 0; (b) 0.6 $\mathrm{dm^3\,min^{-1}}$; (c) 1.3 $\mathrm{dm^3\,min^{-1}}$; (d) 1.8 $\mathrm{dm^3\,min^{-1}}$. 0.03 mol $\mathrm{dm^{-3}}$ acenaphthylene in DMF–$\mathrm{Bu_4NClO_4}$ (0.1 mol $\mathrm{dm^{-3}}$). Zinc cathode 11.5 $\mathrm{cm^2}$.

---

* The flow rates of the electrolyte were measured with a Pitot tube inserted in the upper horizontal connection between the reactor and the reservoir (see Fig. 1).

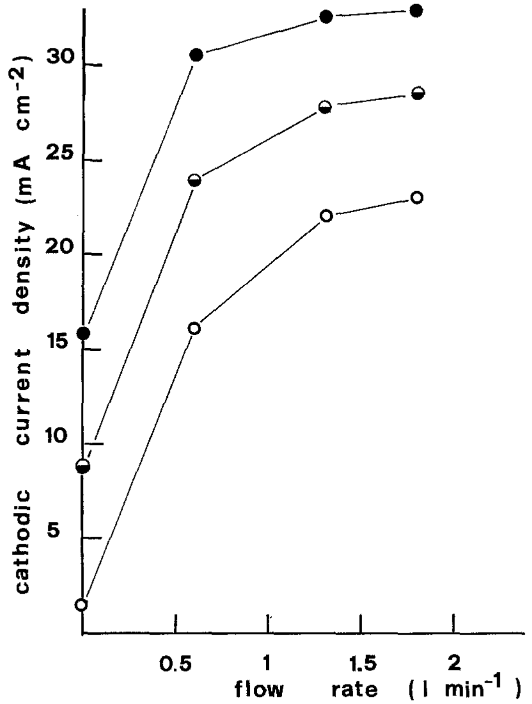


Fig. 5. Dependence of i_{lim} on the flow rate of the electrolyte at different acenaphthylene concentrations: ○, 0.03 mol dm^{-3}; ◒, 0.06 mol dm^{-3}; ●, 0.12 mol dm^{-3}. DMF–Bu_4NClO_4 (0.1 mol dm^{-3}) at 25° C. Zinc cathode 11.5 cm^2.

higher acenaphthylene concentrations. Limiting current densities up to 32 mA cm^{-2} were measured at acenaphthylene concentrations of 20 g dm^{-3} (see Fig. 5).

The preparative experiments confirm these results: at a cathodic current density of 40 mA cm^{-2} excellent yields were obtained, but at 80 mA cm^{-2} only 35% current yield could be reached. As mentioned above, side reactions are the oligomerization of acenaphthylene and, at higher current densities, the cathodic involvement of the solvent and of the supporting electrolyte (see Table 4).

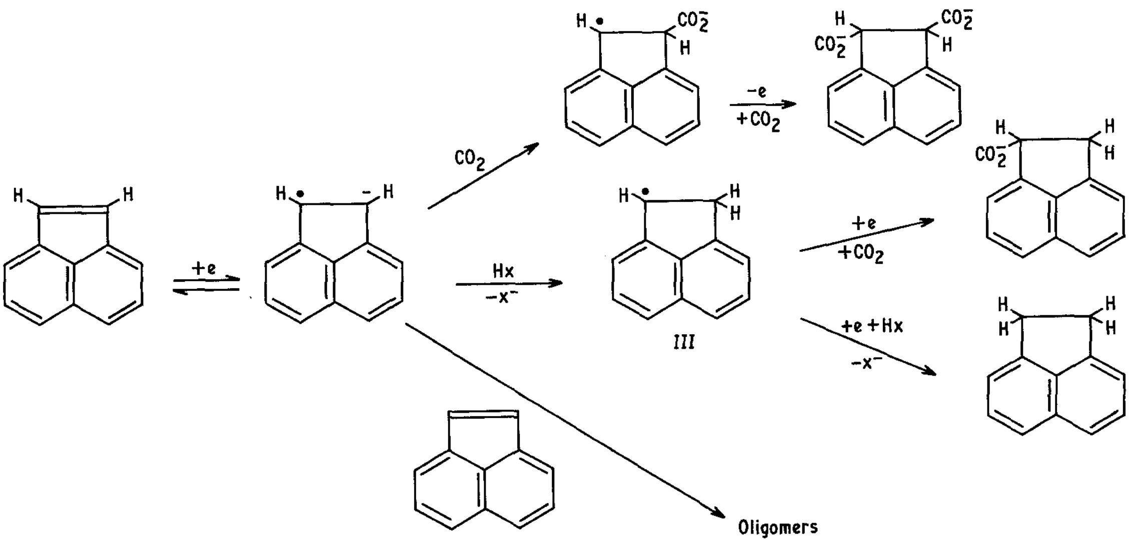
Table 4. Influence of the cathode current density on the dicarboxylic acid yield in large-scale electrolyses

Experiment	*Current density* (mA cm^{-2})	*Current yield* (%)	*Dicarboxylic acid obtained* (g)
1	20	82	103
2	40	80	95
3	60	50	25
4	80	35	30

Anode, zinc; cathode, zinc; 20 g dm^{-3} acenaphthylene (fairly constant concentration) in 1050 cm^3 DMF–Bu_4NClO_4 (0.1 mol dm^{-3}); $T = 25°$ C.

4. Discussion

The carboxylation procedure involves the formation of the anion radical of acenaphthylene which reacts with the Lewis acids present in the medium according to the reaction pattern below. The hypothesis that in the presence of both carbon dioxide and proton donors at fairly similar concentrations only III is formed, is supported by the result that no dicarboxylic acid is found among the products in Experiments 2, 3 and 4 of Table 3.



Carbon dioxide competes with the proton donor only when it has a concentration of nine times that of the Lewis acid.

The following positive aspects of the synthesis may be outlined:

- acceptable cathodic current densities may be employed without appreciable decomposition of the electrolyte even in long-term preparative experiments;
- the yields are not influenced by traces of water;
- elevated pressures of carbon dioxide are unnecessary;
- with aluminium or zinc anodes diaphragmless cells may be used, and separation and work-up of the products are very easy.

This synthesis, which transforms a refinery by-product into a valuable polyfunctional derivative, appears therefore to be a feasible process both on a laboratory-scale and on medium-scale production.

Acknowledgements

This research was supported by the Italian Consiglio Nazionale delle Ricerche, Progetto Finalizzato Chimica Fine e Secondaria, under Contract 80.02160.95.

References

[1] J. H. Wagenknecht, *J. Electroanal. Chem. Interfac. Electrochem.* **52** (1974) 489.

[2] S. Wawzonek and A. Gundersen, *J. Electrochem. Soc.* **107** (1960) 537.

[3] D. A. Tyssee and M. M. Baizer, *J. Org. Chem.* **39** (1974) 2819.

[4] E. Lamy, L. Nadjo and J. M. Savéant, *Nouv. Journ. Chim.* **3** (1979) 21, and references therein.

[5] J. Fisher, Th. Lehmann and E. Heitz, *J. Appl. Electrochem.* **11** (1981) 743.

[6] S. Gambino and G. Silvestri, *Tetrahedron Lett.* **32** (1973) 3025.

[7] J. Canceill and J. Jacques, *Bull. Soc. Chim. Fr.* (1973) 2727.

[8] A. T. Kuhn and R. W. Houghton, 'Topics in Pure and Applied Electrochemistry', SAEST, Karaikudi, India (1975) p. 133, and references therein.