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ELECTROCHEMICAL CARBOXYLATION OF ALDEHYDES AND KETONES WITH SACRIFICIAL ALUMINUM ANODES.

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The electrocarboxylation of aldehydes to the corresponding α-hydroxyacids was described as impossible with conventional electrochemical systems. It is reported here that it is possible to realize it in diaphragmless cells making use of sacrificial aluminum anodes. The method can be used also for the electrocarboxylation of ketones with good yields.

The electrochemical production of α-hydroxyacids from the corresponding aromatic ketones may become a reliable synthetic method, alternative to the chemical ones .The first example of electrocarboxylation of aromatic ketones was proposed by Wawzonek and Gundersen in 1960 (1).Since then several patents and papers have been published (2 - 7) in which consistent improvements of the yields are claimed for the production of compounds having the general formula ArRC(OH)COOH , where R can be either an aromatic or an aliphatic moiety.

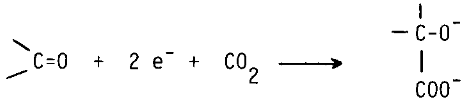
The method, as pointed out by Wawzonek, cannot be applied to aldehydes, neither aromatic nor aliphatic. In the electrocarboxylation of benzaldehyde, hydrobenzoin (30 % yield) was the only isolated product and the rest of the starting material was transformed into tars.

In the course of a systematic investigation on the electrocarboxylation processes we have discovered that, making use of a diaphragmless electrochemical cell with sacrificial aluminum anodes it is possible to perform the electrocarboxylation both of aldehydes and of ketones. The electrochemical system can be schematized as follows .

(anode) Al/ DMF, S.E., CO_2, starting material/ C (cathode)

where : DMF = N,N-dimethylformamide; S.E. = supporting electrolyte (tetrabutylammonium bromide 0.1 M); C = various metals or graphite.

The cathodic process may be represented by the following stoichiometry :



$$>C{=}O + 2\,e^- + CO_2 \longrightarrow \begin{array}{c} | \\ -C{-}O^- \\ | \\ COO^- \end{array}$$

The anodic reaction is : Al → Al(III) + 3 e^-, with a small excess of Aluminum dissolved with respect to this stoichiometry (~5 - 8%).

A bulk reaction of complexation of the hydroxycarboxylate anion on the Al(III) species arising from the anode has the effect of protecting the products from further evolution.

As far as the carboxylation of aldehydes is considered, low yields are obtained with acetaldehyde, whereas more acceptable results were obtained with the aromatic ones.

Among the aromatic ketones the electrocarboxylation of acetonaphtones is reported here for the first time. The reaction is of some applicative interest as the corresponding hydroxyacids are obtained with good yields, and may be used as intermediates for some organic syntheses.

In our opinion this methodology, in which diaphragmless cells are employed, could present some advantages if compared to the use of diaphragm cells or of the preferential oxalate oxidation (2).

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N.	substrate	conc. M 10^{-2}	p CO_2 Atm	V cath./ref.	product yield %	current yield %
1	benzaldehyde	1.5	1	1.1-1.5	31	27
2	benzaldehyde	1.9	1	2.05-2.2	40	35
3	anisaldehyde	1.6	1	1.4-1.6	32	25
4	acetaldehyde	4.4	5	*	9	8
5	2-acetonaphtone	1.9	1	1.35-1.4	80	59
6	6-methoxy-2-aceto naphtone	1.9	1	1.4-1.5	85	73
7	acetophenone	1.8	1	1.45-1.55	62	55
8	benzophenone	1.9	1	1.1-1.2	75	57

solvent : N,N-dimethylformamide; supporting electrolyte : tetrabutylammonium bromide 0.1 M; reference electrode : Ag/AgI/I^- 0.1M ;diaphragmless cells; anode : 99.9 Al, apparent surface : 25 cm^2 ; cathodes : expts. 1 - 4 zinc, 5 - 8 compact graphite, apparent surface 40 cm^2 ; temperature 20 °C.

The isolation of the products was performed by precipitation of the Aluminum salts of the acids by addition of ether to the electrolytic solution, filtration and drying of the salts. Acid hydrolysis of the salts followed by ether extraction gave the crude acids.

* experiment performed under amperostatic conditions.

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