



A Convenient Electrochemical Synthesis of α -Oxoacids

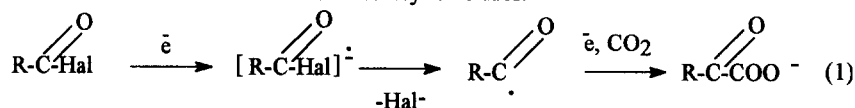
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Summary: The possibility of obtaining aliphatic and aromatic α -oxoacids *via* the direct electrochemical carboxylation of acetyl and benzoyl chlorides has been shown for the first time.

Aliphatic and aromatic α -oxoacids, their esters and salts are being routinely used in organic chemistry, specifically for the synthesis of biologically active substances, drugs, etc. Traditional oxoacid processes¹ are quite often multi-step, require costly reactants, and frequently give low yields of the desired products. It necessitates a search for new alternative ways of synthesizing such compounds.

We supposed that one simple procedure of making α -oxoacids might be the electrochemically activated direct carbon dioxide introduction into acyl chlorides:



Notwithstanding a number of publications regarding electrochemical carboxylation of different organic substrates with CO_2 ^{2,3,4,5}, there are practically no literature data whatsoever on implementing processes proceeding by scheme (1).

In this work we have explored the possibility of producing aromatic and aliphatic α -oxoacids from acetyl and benzoyl chlorides and CO_2 at one step. Pyruvic and benzoylformic acids formed were identified by ^1H NMR spectroscopy⁶, LC, typical reactions with phenyl-, 2,4-dinitrophenylhydrazine and thiosemicarbazide⁷.

Pyruvic acid was electrochemically synthesized from acetyl chloride ($4.2 \cdot 10^{-2}$ M) and CO_2 in an undivided gas-tight cell with platinum cathode (10 cm^2) and sacrificial zinc anode (20 cm^2) in dimethylformamide (DMF) containing 0.1 M Bu_4NBF_4 under a potentiostatic regime ($E=1.1 \text{ V vs Ag/AgCl}$). The solution was carbon dioxide saturated prior to synthesis, with the gas passed throughout the entire process. The process was completed upon passage of electricity calculated from scheme (1). The solvent was distilled under lowered pressure ($p=50 \text{ Pa}$, $t=50^\circ \text{ C}$). On adding HCl to the oil-like residue, the product was ether extracted followed by ether distillation at 20° C . The electrolysis conducted resulted in pyruvic acid with a yield of 60.0 % (Table 1).

Table 1. Yield of α - oxoacids as influenced by the conditions of synthesis.

Substrate	C,M	Electrode material		Electrol. regime	Yield %	Product
		cath.	anod.			
CH ₃ COCl	4.2*10 ⁻²	Pt	Zn	-1.1 V	60.0	CH ₃ COCOOH
-	3.2*10 ⁻²	-	-	-2.0 V	29.6	-
-	4.2*10 ⁻²	-	-	3 mA/cm ²	62.4	-
-	4.2*10 ⁻²	Ni	-	-	35.3	-
-	4.2*10 ⁻²	Pt	Mg	-	35.3	-
-	4.2*10 ⁻²	-	Al	-	26.8	-
C ₆ H ₅ COCl	2.6*10 ⁻²	-	Zn	-	39.0	C ₆ H ₅ COCOOH

Mounting potential up to -2.0 V (potentiostatic regime) leads to a decrease in the yield of pyruvic acid. Such that, going concurrently with acetyl chloride reduction on the cathode may be carbon dioxide reduction, which impedes the progress of the basic process. As follows from Table 1, pyruvic acid can be obtained with sufficiently high yield by carboxylating acetyl chloride not only potentiostatically but galvanostatically as well ($i = 3 \text{ mA/cm}^2$). In the event that use is being made of a magnesium or aluminium anode, pyruvic acid forms, too. Its yield, however, is lower than in the case of a zinc anode.

Parallel with acetyl chloride, we also examined the possibility of cathodic carboxylation of benzoyl chloride. It gives rise to benzoylformic acid with the yield 39% under the synthesis conditions quoted in Table 1.

We think that, similarly to acetyl and benzoyl chlorides, a wide range of other aliphatic and aromatic acyl halides, too, can be electrochemically carboxylated.

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