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ON THE ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE AND ETHYLENE

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Carbon dioxide has been electrochemically reduced to formic acid in aqueous solution[1], to oxalate anion in N,N-dimethylformamide[2,3], and to carbon monoxide in acetonitrile and in dimethylsulfoxide[4].

Ethylene has been reduced to ethane by Kuhn in aqueous solution on platinum[5] and gold[6] electrodes.

Moreover, some electrochemical syntheses of mono and dicarboxylic acids, starting from carbon dioxide and conjugated olefins such as butadiene[7] and α,β-unsaturated carbonylic compounds[2], are quoted in the literature; the only non-conjugated olefins involved in electrochemical syntheses with CO_2 are norbornadiene and dihydropyran[2].

We wish to report now that by electrolysis of a system containing both carbon dioxide and ethylene dissolved under pressure in suitable aprotic solvents it is possible to achieve a direct synthesis of a mixture of oxalic and succinic acids, and that, by means of an adequate control of the partial pressure of ethylene, the synthesis can be directed towards either of the two acids.

Since this is the first example of the electrochemical activation of ethylene in aprotic solvents, we have also investigated the electrochemical behaviour of the same system when CO_2 alone and C_2H_4 alone are present.

a) Electrochemical reduction of carbon dioxide and ethylene

Under the conditions specified in table 1, the electrolysis of a mixture of CO_2 and C_2H_4 dissolved in DMF gives both oxalate and succinate anions; expt. 3 in table 1 shows that the synthesis is practically unfeasible at atmospheric pressure. Significant yields are otherwise obtained at pressures around 20 atm (see table 1); under these conditions the succinate yield increases with the molar fraction of ethylene in the gas phase (see the diagram).

It is noteworthy that the current yield for the oxalate is almost independent of the mole fraction of carbon dioxide in the gas phase in a wide range of compositions.

Tab. 1 - Synthesis of succinic and oxalic acids in DMF

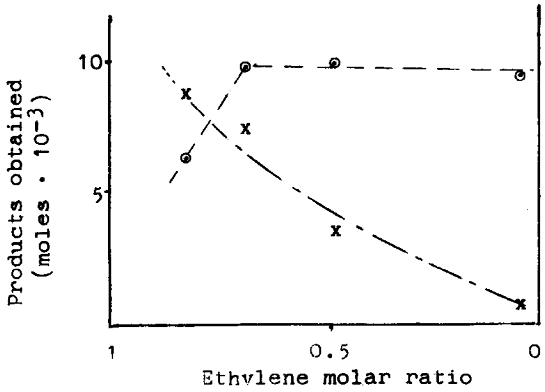
	Cathode[a]	Cathodic current density mA/cm^2	Partial pressures (atm) CO_2	C_2H_4	Products obtained[b] (moles·10^{-3}) oxalate	succinate
1	A	3.4	3.5	16.5	6.3	8.8
2	A	3.4	14.0	0.5	2.6	0.3
3	A	3.4	1.0	2.5	1.4	traces
4	A	30.	4.8	24.2	4.8	9.4
5	B	30	3.4	27.5	2.3	0.9
6	C	33	3.4	24.0	0.7	traces

[a] Cathode: A = stainless steel AISI 316; B = mercury; C = gold.

[b] Electrolyzed residue was evaporated under reduced pressure. Oxalate was recovered from the dried product as the calcium salt, after dissolution in aqueous HCl and precipitation of $Al(OH)_3$. Succinic acid was then recovered from the acidified mother liquors with several ethereal extractions.

Temperature: 20 °C. Solutions were initially 0.1 M in Bu_4NBr.
Circulated charge: 7 · 10^{-2}F. Anode Aluminium 99.9%.

At the end of the electrolyses we have found in the solution significant amounts of carbonates (current yield 25 - 30%), whose presence could have been explained on the basis of the stoichiometry $2\ CO_2 + 2\ e^- \longrightarrow CO + CO_3^=$, proposed by previous authors. However, since in the gas phase we did not find CO, and squarate anion $C_4O_4^=$, which has been described as the main reduction product of CO in the absence of CO_2[8], was not present in the residue, it becomes evident that ethylene modifies the reduction pattern already mentioned, in a way which



Synthesis of oxalic and succinic acids in DMF

Relation between molar ratios of ethylene and carbon dioxide in the gas phase, and the yields of the products. All the experiments were made at initial overall pressure of 20 atm. Current was systematically interrupted after the passage of 7·10^{-2} Faradays.

⊛ : oxalate; x: succinate

will be the object of further studies.

At cathodic current densities suitable for synthetic purposes (30 - 35 mA/cm^2) stainless steel cathodes gave satisfactory yields, while mercury and gold cathodes gave massive solvent reduction and poor yields of conversion.

In HMPA both oxalate and succinate anions are obtained, but this solvent has not yet been fully tested, and a more detailed description will be given later. In THF oxalate anion was obtained, but succinate was not identified.

b) Electrochemical reduction of carbon dioxide

As is shown in table 2, carbon dioxide can be reduced to oxalate anion in DMF, in THF, and in HMPA. Among these solvents, DMF is the best as regards conductivity after the passage of large amounts of charge.

In DMF the CO_2 pressure has a very slight influence on the yield of oxalate anion, but, around atmospheric pressure, polarization phenomena hinder conductivity after the passage of a few thousands coulombs.

In all the experiments mentioned above, CO in the gaseous effluent, and carbonates in the residue were found. However carbonates are in excess in comparison with the stoichiometry already mentioned. For example expt. 3 in table 2 gave: oxalate $1.33 \cdot 10^{-2}$, carbonate $1.8 \cdot 10^{-2}$, carbon monoxide $1.1 \cdot 10^{-2}$; overall current yield (oxalate + carbonate) 85%.

Tab. 2 - Electrochemical reduction of carbon dioxide in aprotic solvents

	Solvent[a]	Pressure (atm)	Charge passed Faraday$\cdot 10^{-2}$	Cathodic current density mA/cm^2	oxalate obtained[b] moles$\cdot 10^{-2}$
1	DMF	1.4	7.7*	3.4	1.5
2	DMF	15.5	23	6.6	4.5
3	DMF	11.5	7.8	3.1	1.3
4	THF	31.0	6.7*	3.4	0.5
5	HMPA	14.8	4.5*	6.6	1.5

[a] DMF = N,N-dimethylformamide; THF = tetrahydrofuran; HMPA = hexamethylphosphoric acid triamide.

[b] Calcium oxalate was precipitated as described in tab. 1.

Temperature - expt. 4: 50 °C; expts 1,2,3,5: 20 °C. - Cathodes, expts 1,2, 4,5: stainless steel AISI 316; expt 3: mercury. - Anodes aluminium 99,9%. Solutions were initially 10^{-1} M in Bu_4NBr.

* Strong polarization phenomena hindered the passage of further charge. The electrolytic cell under pressure is described in ref. 9.

c) Electrochemical reduction of ethylene

When ethylene alone under 15 atm pressure is present in solution, the electrolysis causes an absorption which stops if the current is interrupted. Although the reduction products are still unidentified, a cathodic process involving ethylene is reasonably conceivable, as the weigth loss of the aluminium anode corresponds to the regular oxidation $Al \longrightarrow Al^{3+} + 3\ e^{-}$ within a few per cent. Consequently, in the presence of both carbon dioxide and ethylene only the knowledge of the reduction potential of ethylene in DMF could allow one to make assumptions about which substrate is involved in the cathodic process leading to succinate anion.

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