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An electrochemical cell model of the origin of metabolism

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Abstract

A dynamic system formed by the electrochemical coupling of iron metal and iron-sulphur species, derived from iron sulphide minerals, could promote carbon fixation by reductive carboxylation of thioacetate esters. Using a simple galvanic cell as experimental approach, the results suggest that the electrochemically active interfaces in plausible geochemical conditions could drive a simple proto-metabolism.

1. Introduction

One approach to the study of abiogenesis is the hypothesis of a protometabolic, complex chemical system that precedes the first living beings. The first metabolic systems could emerged from the interaction between sulphide minerals and/or soluble iron-sulphide complexes and fluids rich in inorganic precursors, which are reduced and derived from crustal or mantle activity. The role of iron sulphur proteins (which contain Fe-S clusters as active centers in the electron transfer reactions) and their occurrence in what are possibly the most primitive steps of oxidation of organic substrates, the carbon fixation by reductive carboxylation, and in the cell energy transduction machinery, have been an evidence used to connect the geochemical roots of the origin of life to the origin of biochemistry [1]. The structural similarity between the biological iron-sulphur clusters and the crystal structure of iron sulphide minerals [2], the biomimetic activity of synthetic soluble Fe-S clusters [3] and the highly preserved biochemical reactions involved could explain why Fe-S clusters are found in all biological systems. In this sense, Fe-S clusters could trace the origin of life to the iron sulphide minerals as the roots of biochemistry [4]. In this work, we study the possible connection between the biochemical reductive carboxylation of thioesters and the geochemistry of the iron-sulphide system, by application of a new experimental approach: using an electrochemical cell to simulate how gradients between inorganic species could promote the biomimetic carbon fixation.

2. Results

An electrochemical cell has been constructed using a cylindrical graphite reactor filled with granulated iron metal, a microporous clay barrier and pyrrhotite wet paste formed by pyrrhotite powder, containing 1 mmol of sodium sulphide (pH 9) and, optionally, 1 mmol of hydroquinone. Previously, 1 mmol of ethyl thioacetate was adsorbed by the pyrrhotite powder. A graphite electrode inserted in the pyrrhotite constitutes the cathode. The system was connected to a power supply at 1.1 V under a nitrogen atmosphere. The organic solutes were analysed after three days of standing in anoxic conditions at room temperature; the analysis shows a significant quantity of lactic acid (Figure 1) with an estimated yield of 6.5% of the added ethyl thioacetate. Pyruvic acid was also detected, as well as glycolic acid and glycine.

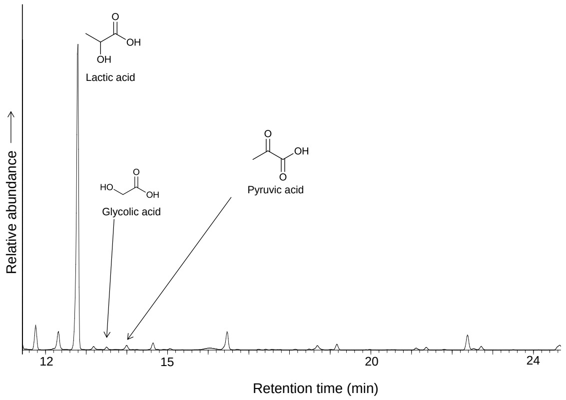

Figure 1: Identified products obtained by carboxylation of ethylthioacetate coupled to the iron/pyrrhotite/sulphide electrochemical system. The major formation of lactic acid could be explained by reduction of newly formed pyruvic acid, catalysed by iron sulphides [5]

The control experiment without an external voltage source shows a significantly lower yield in the formation of lactic acid, suggesting that a low potential electron donor could be necessary for the process. To test this possibility, we performed an experiment using the same electrochemical cell design but without using an external voltage source and adding 1 mmol of hydroquinone ($E^\circ = -0.699V$). Hydroquinone can act as analog of the biological ubiquinol and can perform electron transfer reactions on the surface of minerals [6]. The model biochemical reaction that motivates the selection of hydroquinone as an electron donor is the formation of pyruvate by direct carboxylation of acetic acid, promoted by (quinone) pyruvate dehydrogenase. The presence of hydroquinone promotes the synthesis of lactic acid, increasing the yield to 10.5% and suggesting that electrons can be transferred through iron sulfur clusters or surfaces, similar to the ubiquinol/iron-sulfur system in biochemistry. The experiments performed suggest a model for the reductive carboxylation of thioesters in abiotic and non-enzymatic conditions (Figure 2). Also, an electrochemical cell could be an approach to the experimental study of Origin of Life, as are ideal for the creation of electrochemical gradients and simulate an electrochemically active geochemical interface. Our work is the first experimental use of electrochemical cells within the sphere of abiogenesis and offers a potentially powerful model through which to explore emergent biochemical systems [5].

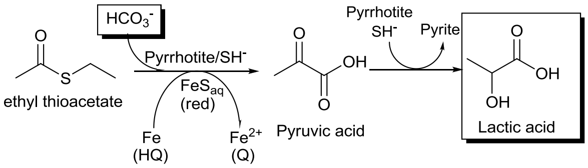

Figure 2: Reductive carboxylation of a simple thioester, pulled by the iron-sulfur system (pyrrothite/FeS/SH^-) in an electrochemical cell. The source of electrons is iron metal. Q: oxidized quinone; HQ: reduced quinone.

3. Summary and Conclusions

Our experimental model shows that pyrrhotite (Fe_7S_8), in a soluble sulphur-rich environment and in the presence of soluble iron-sulphur clusters and newly formed FeS mineral precipitates, whose formation was induced by iron metal anodic oxidation, can promote the reductive carboxylation of simple thioacetic acid esters to form pyruvate/lactate under mild conditions. The reaction could be regarded as biomimetic of the pyruvate synthesis promoted by pyruvate ferredoxin oxidoreductase (PFOR) and favoured by the presence of low potential electron donors, such as hydroquinone, which suggests that the origin of ancient organic cofactors boosted the emergence of simple protometabolic systems. Overall, we showed experimentally that iron sulphides could be coupled with carboxylation in an emerging metabolism by means of an electrochemical gradient.

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