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In this work, the role of iron sulfide minerals and clusters are explored in context of catalyzing and promoting reactions in prebiotic chemistry and in addition, the free energy derived from the hydrolysis of universal and possible prebiotic energy carriers, such as thioesters, is assessed. Three separate research projects are presented, which are divided in Chapter 4 – 6.

Chapter 1, the preamble, serves as an introduction to the field of the origin of life studies at large and highlights one of the hallmarks of life, which is the observation that all life-like systems are far from thermodynamic equilibrium. The three different chemical systems presented here also dissipate energy through an imposed energy gradient, which occurs through either chemical bond breakage (Chapter 5, assessing the free energy contents of high energy compounds), changes in the redox state of molecules (Chapter 3, structural rearrangements coupled to the oxidation of $Fe^{2+}S$) or the self-assembly of small constituents into larger systems (Chapter 4, thioester synthesis coupled to FeS mineral formation and peptide ligated [FeS] cluster formation).

An introduction to the origin of life theory of the "iron-sulfur world" is given in Chapter 3, which encompasses the reduction of CO_2 through (i) coupling to the oxidation of mackinawite ($Fe^{2+}S$) to pyrite (FeS_2), (ii) redox gradients generated at hydrothermal vents, together with simulated hydrothermal conditions in laboratory experiments, and (iii) synthetic [FeS] cluster analogues. In brief, both Nernstian gradients generated on metal sulfide interfaces and $Fe^{2+}S$ oxidation to FeS_2 can facilitate CO_2 reduction under simulated hydrothermal conditions and several C_2 to C_4 compounds (i.e. pyruvate, butanethiol and ethanol) have been obtained under various degrees of reducing conditions. FeS minerals – and in particular Fe(Ni)S – allow for the synthesis of a variety of organic compounds found in biochemistry and might also allow for the creation of self-assembled and self-replicating chemical networks akin to the CO_2 fixating Wood-Ljungdahl pathway or the reverse tricarboxylic acid cycle found in extant biology.

Chapter 4 is concerned with the characterization of the electronic transitions of $Fe^{2+}S$ under oxidizing conditions and the development of a redox catalyst that facilitates redox transitions similar to biological [FeS] clusters, namely the reversible redox of sulfide ligated Fe^{2+}/Fe^{3+}. The resulting electrode material is characterized via cyclic voltammetry, Raman and X-ray absorption spectroscopic techniques. Tracing oxidative maturation pathways by varying electrode potential, nanoparticulate $n(Fe^{2+}S^{2-})_{(s)}$ was found to oxidize to a Fe^{3+} containing FeS phase at -0.5 V vs. Ag/AgCl (pH = 7). In a subsequent oxidation, polysulfides are proposed to give a material that is composed of Fe^{2+}, Fe^{3+}, S^{2-} and polysulfide (S_n^{2-}) species. The composition of this electrode material is described as $Fe^{2+}{}_{1-3x}Fe^{3+}{}_{2x}S^{2-}{}_{1-y}(S_n^{2-})_y$. The thermodynamic differences between ligand- and metal-based oxidation processes were calculated by density functional theory as to rationalize the possible electronic and structural interconversions.

Chapter 5 investigates the synthesis of "high-energy' thioesters from thioacetic acid in the presence of

ferrous and ferric iron. Three distinct reaction pathways are identified, which involve (i) the oxidation of thioacetic acid to acetyldisulfide, (ii) the degassing of sulfide under acidic conditions, which drives the reaction to the side of the products, and (iii) the sequestration of sulfide in the form of mackinawite, which also increases the reaction yields. Furthermore, [FeS] clusters can be reconstituted in the presence of a ferredoxin-like peptide sequence, which also exhibit redox activity. These results combined open an avenue into the one-pot synthesis of redox-mediators in the form of [FeS] clusters and high-energy thioester bonds under prebiotic conditions, which both constitute important constituents of metabolisms.

In Chapter 6, the Gibbs free energies of hydrolysis of thioactic acid, methyl-thioacetate, pyrophosphate, triphosphate and adenosine triphosphate are assessed in respect to the hydrolytic stability of each compound under variable pH and temperature conditions. In brief, thioacetic acid and methyl-thioacetate are the preferred energy carriers at pH 7 and pH 5 respectively and at temperatures above 45°C, due to their higher hydrolytic stability compared to phosphoesters. Phosphoesters on the other hand exceed in their available free energy at lower temperatures and at alkaline conditions. A selection of these energy carriers could have therefore occurred on the early earth based on the environmental parameters, i.e. sulfur-containing compounds could have been preferred under slightly acidic, hydrothermal conditions.

The last chapter briefly summarizes the above findings and proposes a reaction system, which builds on the experimental results gathered in the previous chapters. This reaction system involves the use of an oxidized $Fe^{2+}S$ electrode as a source of polysulfides, which are proposed to sulfidize crotononitrile to 3-mercaptobutanimidothioic. This thiol containing thioacid in turn is proposed to produce thioesters through the reaction of the mercapto-group, stemming from a second molecule, with the thioacid residue, possibly producing a thioester polymer. If the production of polysulfides can be controlled via the applied electrode potential, thioester and thioacid formation can then be directly coupled to a controlled redox reaction.