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論文審査の要旨(2000 字程度)

This thesis entitled "The Role of Iron Sulfide Minerals and Sulfur-containing Organic Compounds in Prebiotic Chemistry" is composed of seven chapters.

Chapter 1 "Preamble" serves as an introduction to the field of the origin of life studies at large and highlights the observation that all life-like systems are far from thermodynamic equilibrium. The three different chemical systems presented here dissipate energy through an imposed energy gradient, which occurs through either chemical bond breakage, changes in the redox state of molecules, or the self-assembly of small constituents into larger systems.

Chapter 2 "Abstract" contains the role of iron sulfide minerals and clusters explored in the 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.

Chapter 3 "Introduction" summarizes the theory of the "iron-sulfur world" 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 $[\text{FeS}]$ cluster analogues. In brief, both potential 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 have been obtained under various degrees of reducing conditions. FeS minerals 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 fixing pathway or the reverse tricarboxylic acid cycle found in extant biology.

Chapter 4 "The electrochemical properties of iron(II) sulfide" 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 $[\text{FeS}]$ clusters, namely the reversible redox of sulfide ligated $\text{Fe}^{2+}/\text{Fe}^{3+}$. 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 was found to oxidize to a Fe^{3+} containing FeS phase.

Chapter 5 "Simultaneous synthesis of thioesters and $[\text{FeS}]$ clusters from thioacetic acid" 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 acetyl disulfide, (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, $[\text{FeS}]$ clusters can be reconstituted in the presence of a ferredoxin-like peptide sequence, which also exhibits redox activity. These results open an avenue into the one-pot synthesis of redox-mediators in the form of $[\text{FeS}]$ clusters and high-energy thioester bonds under prebiotic conditions.

Chapter 6 "Assessment of free energy availability from ester hydrolysis in prebiotic scenarios" discusses the Gibbs free energies of hydrolysis of thioacetic acid, methyl-thioacetate, pyrophosphate, triphosphate and adenosine triphosphate 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. Selections 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.

Chapter 7 "Conclusion and Outlook" 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. 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.

This thesis contains original and valuable scientific results and contributes to new insights of the origin of life studies and prebiotic chemistry. Therefore this thesis is considered to be of sufficient value for the doctor's degree of science.

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