

Iron mediated synthesis of thioesters with thioacetic acid and simultaneous formation of FeS clusters in aqueous solution

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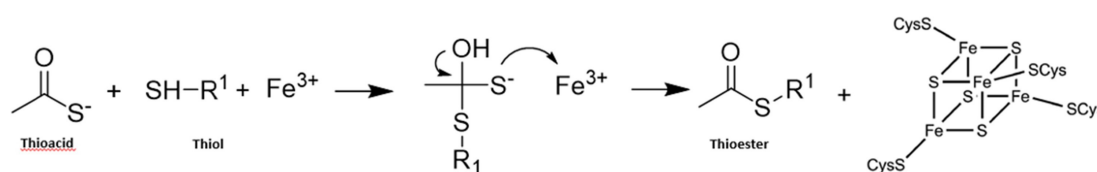
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In biological systems, endergonic reactions such as peptide bond formation are coupled to the hydrolysis of phosphoesters (such as ATP) which have a high free energy of hydrolysis. A further hallmark of biology is that the maintenance of high NTP/NDP ratios in the cell is coupled to electron transfer reactions. Here we report new work showing that thioesters can be synthesized from thioacetic acid in a reaction that simultaneously leads to the formation of redox active FeS clusters (Scheme 1).

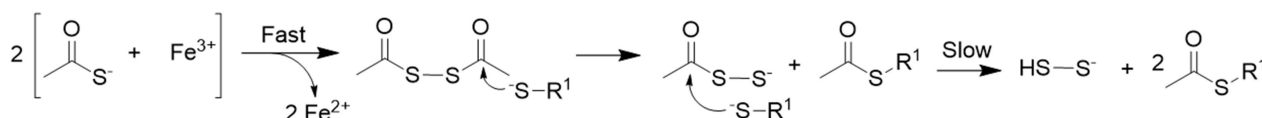
A pH below 7 and the subsequent degassing of hydrogen sulfide produced during the reaction has been found to drive the otherwise thermodynamically unfavorable reaction, in which a thioacid with a standard free energy of hydrolysis of -15 kJ mol^{-1} is converted to a thioester with a free energy of -37 kJ mol^{-1} . The energy conversion from thioacids to thioesters in terms of free energies of hydrolysis can be as high as 52% if the thiol participating in the reaction incorporates a tertiary amine functional group that additionally accelerates the reaction. When this reaction is then coupled to the oxidation of thioacetate by ferric iron (Scheme 2), thioester yields of up to 47% can be achieved in respect to the amount of thioacetic acid added and the reaction reaches its highest concentration within one hour.

The sulfide produced during the generation of thioesters from thioacids reacts with ferric iron in solution which results in the starting materials for the reconstitution of $[\text{Fe}_4\text{S}_4]$ clusters that are frequently employed in biology to facilitate redox reactions; thus providing a possible prebiotic route to ester exchange, polymerization, and electron transfer reactions.

Keywords: Origin of Life, Thioester synthesis, FeS cluster



Scheme 1. Thioester synthesis and simultaneous iron sulfur cluster formation.



Scheme 2. Thioester synthesis via the oxidation of thioacetate