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## CARBOHYDRATES AS A SOURCE OF ENERGY AND MATTER FOR THE ORIGIN OF LIFE

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One of the most important questions concerning the origin of life is the nature of the primitive process that provided the chemical energy necessary for the emergence of biological complexity. We have approached this question by studying chemical reactions that resemble glycolysis in the way they yield useful chemical energy. The central role of glycolysis in metabolism plus its ability to function under the anaerobic conditions of early Earth suggest that it may have provided the energy needed for the origin of life. Our chemical studies have focused on the first energy-yielding step of glycolysis involving the oxidation of glyceraldehyde-3-P which initially yields an 'energy-rich' glyceroyl enzyme thioester that drives the synthesis of ATP via a 1,3-diphosphoglycerate intermediate. Our previous nonenzymatic studies established that glyceraldehyde oxidation in the presence of a thiol yields 'energy-rich' thioesters and that thioesters can act as condensing agents for the synthesis of phosphoanhydrides.

Recently, we proposed a new model of early glycolysis in which the oxidation of glyceraldehyde self-hemiacetals yielded 'energy-rich' polyglyceric acid instead of 'energy-rich' thioesters. In this model, polyglyceric acid not only acts as an energy source for phosphoanhydride synthesis, but also as an autocatalyst that can replicate the sequence of D- and L-residues in its structure. We began our investigation of this new hypothesis - the triose model - by developing a thermal method for the racemization-free synthesis of polyglyceric acid. The hydrolytic stability and the role of chirality in interactions of polyglyceric acid were studied using this thermal polymer. Next, we established that the the 2- and 3-glycerol esters of polyglyceric acid are 'energy-rich' by measuring the Gibbs free energy change of hydrolysis ( $\Delta G^\circ$ , pH 7) of the 2- and 3-glycerol esters of 2- and 3-O-L glyceroyl-glyceric acid methyl ester -- a model of polyglyceric acid. The  $\Delta G^\circ$  of 2- and 3-glycerol esters were -9.1 kcal/mol and -7.8 kcal/mol, respectively. Recently, we discovered 1) that glyceraldehyde is bound and oxidized to glyceric acid on the surface of ferric hydroxide, and 2) that soluble ferric ion catalyzes the rearrangement of glyceraldehyde to lactic acid. We are exploring the possibility that these reactions could yield polyglyceric acid and polylactic acid under plausible prebiotic conditions.