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The Effects of Metal Ions on Reactions of Thioesters in Simulated Prebiotic Environments

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Reactions of Thioesters: The ‘Thioester World’ model posits that thioesters were a key functional group at some point in the development of life on Earth.¹ We are interested in studying the kinetics of reactions of thioesters, shown in Figure 1, to evaluate their prospective roles in prebiotic chemistry. Previously, we reported kinetics for hydrolysis and thiol-exchange reactions of model thioesters in buffered water.² Given that the prebiotic ocean was unlikely to have resembled such a clean system, we have begun to explore the effects of various metals on the hydrolysis, aminolysis, and thiol–thioester exchange reactions of thioesters in more complex aqueous solutions. These solutions include Na⁺, K⁺, Mg²⁺, Ca²⁺, Fe²⁺, Mn²⁺, and Co²⁺, all of which are conjectured to have been present in the ancient ocean.³ The kinetics of the reactions are monitored using ¹H NMR spectroscopy.

Analysis of ¹H NMR Samples with High Paramagnetic Ion Concentrations: Many prebiotic chemistry models invoke conditions in which reaction mixtures are subjected to wet–dry cycles of hydration (e.g., by rain) and evaporation. The process of evaporation introduces the potential for significantly higher concentrations of metal ions than in the larger prebiotic ocean. When present in substantial concentration, the ions that are paramagnetic (Fe²⁺, Mn²⁺, and Co²⁺) can render NMR spectroscopy impracticable from the broadening of the signals in the spectra. In addition to the study of the kinetics of the hydrolysis, aminolysis, and thiol–thioester exchange reactions, we developed a method that allows the use of ¹H NMR spectroscopy to observe prebiotically relevant organic compounds in aqueous solutions containing paramagnetic metal ions.

References: [1] De Duve, C., *Blueprint for a cell: the nature and origin of life*. N. Patterson: Burlington, N.C., 1991; p 275. [2] Bracher, P. J.; Snyder, P. W.; Bohall, B. R.; Whitesides, G. M., *Abstr Pap Am Chem S* **2011**, *41*, 399-412. [3] Anbar, A. D., *Science* **2008**, *322* (5907), 1481-1483.

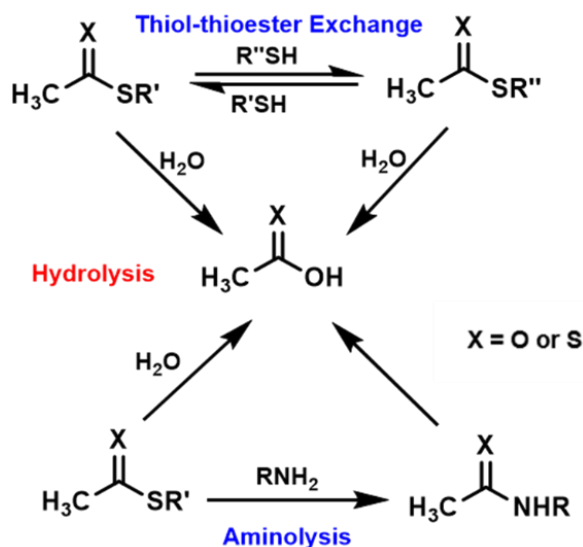


Figure 1. Thiol–thioester exchange, aminolysis, and the competing hydrolysis reaction in water