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Kinetic study of GlyGly formation under condition simulating the ion composition of Lost City alkaline hydrothermal vent

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Introduction: Based on that the dissociation behaviors of amino acids are highly influenced by pH of the solution, we have previously revealed that the dimerization of Gly dimerization reached the maximum rate in alkaline solution of pH 9.8 (Sakata et al., submitted). Recently, an alkaline hydrothermal system was discovered in Lost City hydrothermal field in the Mid Atlantic Ridge (Kelly et al. 2001; 2005). The hydrothermal system is suggested as a plausible environment for the origin and evolution of life in the early Earth (Russell 2003). To understand the chemical evolution pathways of biomolecules, determination of reaction constants are necessary. In this study, GlyGly formation and decomposition were kinetically investigated through the heating experiments of glycine at various temperatures under conditions simulating the ion composition of Lost City alkaline hydrothermal system.
Experimental: Eight milliliter of 100 mM Gly solutions of pH 9.3 with $MgCl_2$(9.4 mM), $MgSO_4$(4.6 mM), $CaCl_2$(23mM), NaCl (35 mM) and NaOH (470 mM) (Solution A) were put into Teflon bottles and heated at 120, 140, 160 and 180 degrees C for 1 to 5 days. After heating, each sample was 10 times diluted and analyzed by High Performance Liquid Chromatography (HPLC). 100 mM Gly solutions of pH 9.3 with only NaOH (Solution B) and 100 mM Gly solution of pH 7.1 with only NaOH (Solution C) were heated at 140 degrees C for comparison. In this study, there are four possible reaction pathways: Gly to GlyGly (the second order), GlyGly to DKP (the first order), DKP to GlyGly (the first order), GlyGly to Gly (the first order). The data from the heating experiments were fitted to the four reactions to obtain the rate constants.
Results and discussion: The formation rates of GlyGly in Solution A (1.25 10^{-9}l $mol^{-1}s^{-1}$) and B (0.93 10^{-9}l $mol^{-1}s^{-1}$) were similar. Decomposition rates of GlyGly in Solution A (2.49 10^{-5}mol $l^{-1}s^{-1}$) and B (1.33 10^{-5}mol $l^{-1}s^{-1}$) were also similar. However, the amount of GlyGly in Solution A at equilibrium was 25 percent smaller than that in Solution B. These results indicate that in the alkaline solution, the formation of GlyGly is inhibited in the presence of metal ions such as Mg^{2+},$Ca^{2+}$and Na^{+}. On the other hand, the formation rate and amount of GlyGly in Solution C (4.61 10^{-11}l $mol^{-1}s^{-1}$) were much smaller than that in Solution A, implying that the alkaline solution promotes GlyGly formation despite lowering of the reaction rate by the metal ions. The amount of DKP in Solution A at equilibrium was 18 percent smaller than that in Solution B. The formation rate of DKP in Solution A (5.05 $10^{-4}s^{-1}$) was 8 times higher than that in Solution B (0.649 $10^{-4}s^{-1}$). The decomposition rate of DKP in Solution A (5.22 $10^{-3}s^{-1}$) was 7 times higher than that in Solution B (0.71 $10^{-3}s^{-1}$). These results suggest that in the alkaline hydrothermal vent like Lost City, promotion of GlyGly formation by the pH effect is more favorable than inhibition of the reaction by metal ions in the seawater.
References:
Kelley DS et al., (2001) Nature 412:145-149
Kelley DS et al., (2005) Science 307:1428-1434
Russell MJ (2003) Science 302:580-581

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