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Effects of calcium chloride on the dimerization rate of glycine in aqueous solution

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Introduction:
The Lost City hydrothermal field has been recently discovered in 2000 and known for its characteristic conditions that differs from the typical hydrothermal vents, such as basic pH, low temperature ($>$ ˜90^{o}C), metal ion compositions (Kelley 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). In our previous study, it was revealed that the dimerization of glycine (Gly) in aqueous solution reached the maximum rate in basic solution at pH 9.8 (Sakata et al., 2010), supporting the above hypothesis. In this study, the heating experiments of Gly solution containing calcium chloride were conducted under various pH conditions, in order to evaluate the effects of calcium chloride on the kinetics of the formation of glycylglycine (GlyGly) and diketopiperazine (DKP).

Experimental:
Half milliliter of 100 mM aqueous solutions of Gly at pH 2.3, 6.0 and 9.8 with 200 and 400 mM $CaCl_2$ and without $CaCl_2$ were put into pyrex glass tubes, vacuumed and replaced with Ar gas. Each solution was heated at 140^{o}C for 1 to 14 days. Each sample was 10 times diluted and analyzed by High Performance Liquid Chromatography (HPLC). In this experiment, the four reaction pathways were considered: 2 Gly to GlyGly (the second order), GlyGly to DKP (the first order), DKP to GlyGly (the first order), GlyGly to 2 Gly (the first order). The rate constants were determined by fitting the changes of the concentrations of Gly, GlyGly, and DKP with increasing heating time.

Results and discussion:
Equilibrium concentration of GlyGly decreased with increasing concentration of calcium ion at acidic and basic pH. At neutral condition, concentration of GlyGly was almost constant. Dimerization rates of Gly (k_1) were decreased by $CaCl_2$ at pH 2.3, 6.0, while at pH 9.8, that slightly increased with increaseing concentration of calcium ion. The same way as Gly solution without $CaCl_2$, k_1 was fastest at pH 9.8 in Gly solution with $CaCl_2$.
However, at pH 9.8, hydrolysis rate of GlyGly (k_{-1}) was much larger than that of k_1, which likely caused the lower concentration of GlyGly. Thus, in particular at basic pH, $CaCl_2$ drives hydrolysis of GlyGly. This is probably due to the complex formation of GlyGly with calcium ion where hydroxyl ion easily hydrolyzes the peptide link.

References:
Kelley et al. (2001) Nature 412:145-149
Kelley et al. (2005) Science 307:1428-1434
Russell (2003) Science 302:580-581
Sakata et al. (2010) Geochim Cosmochim. Acta 74, 6841-6851.

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