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Research Article

Peptide Synthesis in Early Earth Hydrothermal Systems

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Abstract

We report here results from experiments and thermodynamic calculations that demonstrate a rapid, temperature-enhanced synthesis of oligopeptides from the condensation of aqueous glycine. Experiments were conducted in custom-made hydrothermal reactors, and organic compounds were characterized with ultraviolet-visible procedures. A comparison of peptide yields at 260°C with those obtained at more moderate temperatures (160°C) gives evidence of a significant (13 kJ · mol^{-1}) exergonic shift. In contrast to previous hydrothermal studies, we demonstrate that peptide synthesis is favored in hydrothermal fluids and that rates of peptide hydrolysis are controlled by the stability of the parent amino acid, with a critical dependence on reactor surface composition. From our study, we predict that rapid recycling of product peptides from cool into near-supercritical fluids in mid-ocean ridge hydrothermal systems will enhance peptide chain elongation. It is anticipated that the abundant hydrothermal systems on early Earth could have provided a substantial source of biomolecules required for the origin of life. Key Words: Origin of life—Hydrothermal—Peptide—Condensation—Hydrolysis—Gibbs energy. Astrobiology 9, 141–146.

1. Introduction

The thermal stability of peptides and proteins in thermophilic microorganisms is controlled by the temperature-dependent equilibrium between the bonded amino acid (*i.e.*, oligopeptide) and the non-bonded form (Radzicka and Wolfenden, 1996; Amend and Helgeson, 2000). Similarly, elongation of small peptides toward proteins on early Earth would have been subject to the same thermodynamic conditions (Imai *et al*., 1999). The possible connection between this temperature effect and the occurrence of biomolecules in present-day hydrothermal systems has prompted some to hypothesize that life may have emerged from a deep-sea hydrothermal environment (Shock, 1996; Huber *et al*., 2003). This connection is also supported by the high-temperature bacterial rooting of the tree of life (Pace, 1991; Di Giulio, 2001).

Thermodynamic calculations undertaken to model the thermal stability of peptides at elevated temperatures (Shock, 1992) revealed that increasing temperatures shift the equilibrium between the amino acids *a*, or amino acid *a* and oligopeptides a_n and a_{n+1}, according to

$$a + a_n = a_{n+1} + H_2O \quad (1)$$

toward condensation with fundamental prebiotic implications (Holm and Andersson, 2005; Russell *et al*., 2005). Shock (1992) also demonstrated that such an exergonic shift would translate into a cumulative increase in product peptides that, in return, would feed into the next condensation step and, thus, promote peptide chain elongation. Conversely, at lower temperatures, this thermodynamic restriction would lead to a decline in product peptides that would effectively terminate the chain elongation process (Dose, 1975).

The theory of a hydrothermal origin of life is founded on the postulate that temperature increases along geothermal gradients induce a thermochemical favor for oligomerization over hydrolysis, for instance, high-temperature amino acid condensation over peptide bond rupture (Shock, 1992; Plyasunov and Shock, 2001). As an example, a temperature increase from 25°C to 374°C is predicted to lower the free energy of peptide bond formation in diglycine (gly_2) from glycine (gly) by around 9 kJ · mol^{-1} (2 gly ⇔ $gly_2 + H_2O$; $\Delta G_{25°C} = 14.2$ kJ · mol^{-1} while $\Delta G_{374°C} = 5.0$ kJ · mol^{-1}). Building on the work by Wächtershäuser (Huber and Wächtershäuser, 1998) and Shock (Shock, 1992, 1996), Matsuno and coworkers demonstrated that, when solutions containing amino acids are circulated from cold (4°C) into hot

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(225°C) regions of a flow-through reactor, oligopeptides are formed (Imai *et al*., 1999). From these experiments, it appears that the residence time of the amino acid solution in the high-temperature reactor section of the flow-through reactor strongly influenced peptide yields (*i.e.*, extending the residence time resulted in higher peptide levels). However, these experiments were conducted with heating time periods of around 30 to 80 seconds, and it remains unclear how the thermal stability of peptides changes as the heating period is extended. The experimental results presented here provide substantial support for the high-temperature stability of peptides (Shock, 1992; Imai *et al*., 1999). Specifically, we have considered the oligomerization of glycine according to Eq. 1 in the temperature range 160–260°C and 200 bar pressure, conditions typical of deep-sea hydrothermal vents.

2. Methods

Our experiments were conducted in custom-made gold (Au) hydrothermal reaction cells (Rosenbauer *et al*., 1993) that were loaded with preheated, degassed, and pH buffered solution (phosphate salt buffer at pH 6.85). The hydrothermal cells were constructed of flexible inert Au and could be applied up to supercritical temperatures and pressures as well as extreme pH conditions. All components of the Au cell were pretreated with a 6 *N* HCl solution at 90°C and baked at 600°C for 6 hours to remove surface contaminants. Amino acid stock solutions were injected via high-pressure ISCO syringe pumps into the preheated fluid and sampled at regular intervals. Quantitative analysis of glycine and its peptides was performed by high-pressure liquid chromatography and ultraviolet-visible (205 nm) detection. Amino acid and peptide samples were analyzed with a Waters 490E HPLC apparatus with use of a Hypersil 5 mm, 250 × 4.6 mm ODP column and a 10 mmolal NaH_2PO_4 and 5 mmolal $NaC_6H_{13}SO_3$ mobile phase maintained at pH 2.6 by addition of H_3PO_4. Carbon dioxide was analyzed by coulometric titration.

3. Results

Our measured trends in concentrations of glycine and product peptides at 160, 220, and 260°C, which are shown in Fig. 1, contrast significantly with results from experiments conducted in Au and Ti (Qian *et al*., 1993), Ti (Li and Brill, 2003), quartz (SiO_2) (Snider and Wolfenden, 2000), and Inconel Ni-Cr-Fe alloy reactors (Sato *et al*., 2004) (thin broken lines in Fig. 1). Results of our experiments demonstrate the formation of small peptides from glycine in hydrothermal solutions, whereas previous studies in metal-alloy or quartz cells demonstrated that glycine undergoes rapid decarboxylation only and does not form peptide bonds (see colored dashed lines in Fig. 1). The rapid decarboxylation rate of glycine is due, in part, to the fact that this type of work is usually performed in highly reactive metal reactors where it is difficult to control variables that affect biomolecule stability, such as reactor wall catalysis (Brill, 2000), reactor corrosion (Maslar *et al*., 2002), as well as metal elution (Faisal *et al*., 2004). Note that a similar surface effect has recently been observed for glycine but also for other amino acids such as alanine (Cox and Seward, 2007).

We infer that in inert Au cells glycine undergoes parallel decarboxylation and oligomerization; at 160°C, 0.05% of glycine is converted to diglycine, and diglycine concentration levels represent 43% of total product dimer (Fig. 1A). At

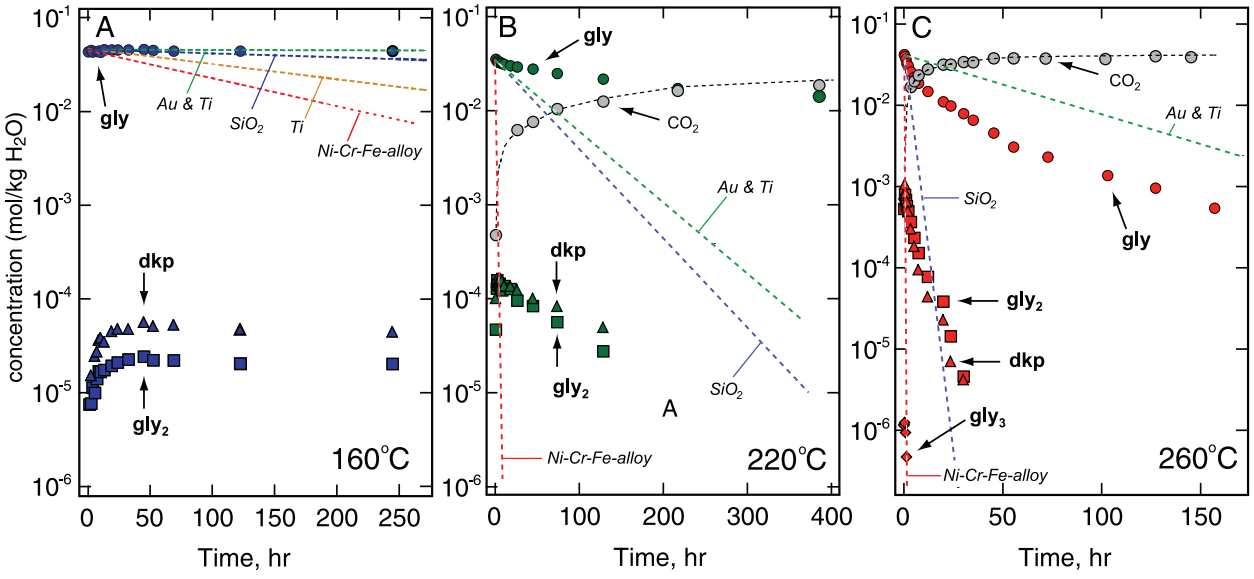

FIG. 1. Decarboxylation rates of glycine in different reactor types and the formation of small peptides in gold cells. Shown are glycine (●), diglycine (■), diketopiperazine (▲), triglycine (◆), and CO_2 concentration-time profiles at (**A**) 160°C, (**B**) 220°C and (**C**) 260°C and 200 bar. Also shown are decarboxylation profiles for glycine in Au and Ti (Qian *et al*., 1993), Ti (Li and Brill, 2003), quartz (Snider and Wolfenden, 2000), and Inconel Ni-Cr-Fe alloy (Sato *et al*., 2004) reactors, projected applying reported activation energies and frequency factors that demonstrate surface-induced glycine decarboxylation. Dashed lines through measured CO_2 data are projected CO_2 concentrations calculated from measured glycine loss.

220°C, diglycine concentrations relative to glycine are substantially higher, but diketopiperazine yields relative to diglycine are reduced compared to 160°C (Fig. 1B). At 260°C, glycine dimerization relative to glycine is favored with increasing temperature from 220°C, whereas the yields of diketopiperazine relative to diglycine are reduced over the same temperature range (Fig. 1C). Peptide elongation toward triglycine (Fig. 1C) was observed only at the highest temperatures (*i.e.* 260°C). Decarboxylation of glycine was observed at 220 and 260°C, but no CO_2 was detected at 160°C. Similarly, we were not able to detect product acetate and ammonia that would evolve from glycine deamination.

4. Discussion

To understand our experimental results, we calculated the energetics of peptide bond formation using the standard Gibbs energies of reaction in conjunction with observed concentration ratios. The change in energy associated with peptide synthesis is calculated from the relationship

$$\Delta G_r = \Delta G_r^0 + RT \ln Q_r \tag{2}$$

where ΔG_r, ΔG_r^0, and Q_r represent the Gibbs energy change of reaction, the standard-state Gibbs energy of reaction, and the activity product quotient, respectively; R is the gas constant, and T is the temperature in units Kelvin. The standard state convention used here is unit activity in a hypothetical 1 molal solution for aqueous species with reference to an infinite dilution at any temperature and pressure, and the standard state for H_2O is unit activity of pure water at any temperature and pressure. Note at equilibrium $\Delta G_r = 0$, thus

$$\Delta G_r^0 = -RT \ln Q_r \tag{3}$$

and measured values of Q_r may be applied to calculate the standard molal Gibbs energy of reaction ΔG_r^0. Values of Q_r needed to calculate ΔG_r^0 are obtained from the expression

$$Q_r = \Pi\, a_i^{v_{i,r}} \tag{4}$$

where a_i stands for the activity of the i^{th} species and $v_{i,r}$ denotes the stoichiometric reaction coefficient (negative for reactants, positive for products). Assuming unity for the ratios of activity coefficients for all species in Eq. 1, values of ΔG_r^0 are readily obtained from experimental observations (Fig. 1) and may be compared with theoretical values of ΔG_r^0 computed with use of thermochemical properties and parameters for the Helgeson-Kirkham-Flowers (HKF) equation of state (Helgeson *et al.*, 1981) together with the SUPCRT92 software package (Johnson *et al.*, 1992). Shock (1992) provided a detailed description of the revised HKF equation of state for standard partial molal volumes and heat capacities for aqueous organic compounds.

Values of $-RT \ln Q_1$ (Q_1 refers to the activity product quotient for the glycine dimerization reaction 2gly = gly_2 + H_2O, see Fig. 2A) and $-RT \ln Q_2$ (here Q_2 refers to the activity product quotient for the glycine cyclization reaction 2gly = diketopiperazine + $2H_2O$, see Fig. 2B) were calculated with use of measured glycine and oligoglycine concentrations (Fig. 1) and are shown in Fig. 2 as a function of time. Note that values of $-RT \ln Q_1$ for glycine dimerization are endergonic and are shifted to lower values with increasing temperature (Fig. 2A). At time periods larger than 10–15 hours, values of $-RT \ln Q_1$ decrease with increasing temperature from 16.0 (±0.9) kJ · mol^{-1}, to 7.9 (±1.3) kJ · mol^{-1}, to 2.9 (±1.9) kJ · mol^{-1} for experiments at 160, 220, and 260°C, respectively. Thus, temperature increases along fluid flow paths in hydrothermal systems would correspond to an increase in the thermodynamic stability of the peptide bond in diglycine. Furthermore, it can be seen in Fig. 2B that formation of diketopiperazine from glycine is equally endergonic at 160°C, and values of $-RT \ln Q_2$, similar to those obtained for glycine dimerization, are shifted to lower values with increasing temperature. Values of $-RT \ln Q_2$ for the cyclization reaction that forms diketopiperazine decrease from 12.9 (±1.1) kJ · mol^{-1} through 8.0 (±1.9) kJ · mol^{-1} to 3.0 (±2.5) kJ · mol^{-1} for temperatures 160, 220, and 260°C (Fig. 2B). We have concluded that diketopiperazine is thermodynamically more stable relative to glycine with increasing temperature in hydrothermal environments. It should be noted in Fig. 2 that steady-state time periods in the higher-temperature runs, *i.e.*, 260°C, are significantly shorter by tens of hours than at, for instance, 160°C, which is directly attributable to the accelerated decarboxylation of glycine at the higher temperature.

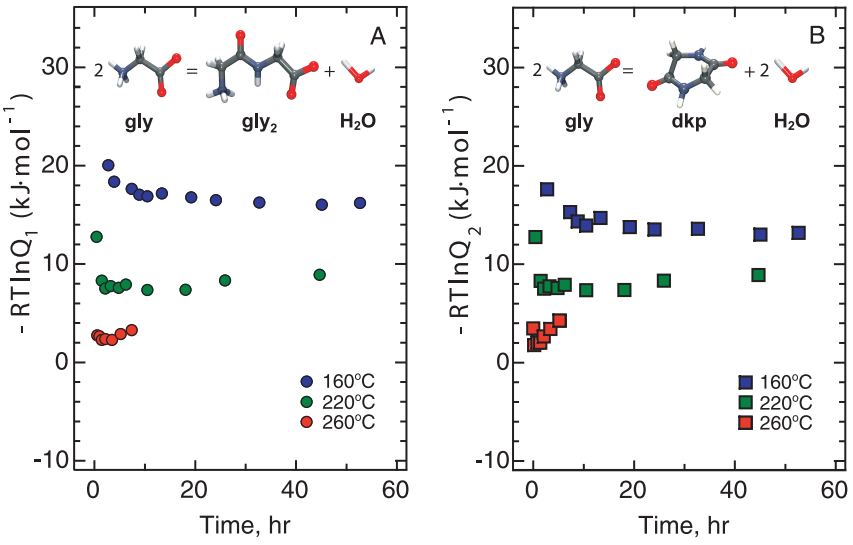

FIG. 2. Effective free energy of peptide synthesis as a function of time. Values of $-RT \ln Q_r$ for (**A**) glycine dimerization ($-RT \ln Q_1$) and (**B**) diketopiperazine synthesis ($-RT \ln Q_2$) from glycine at 160°C (blue), 220°C (green), 260°C (red) and 200bar. Error bars are smaller than symbol size.

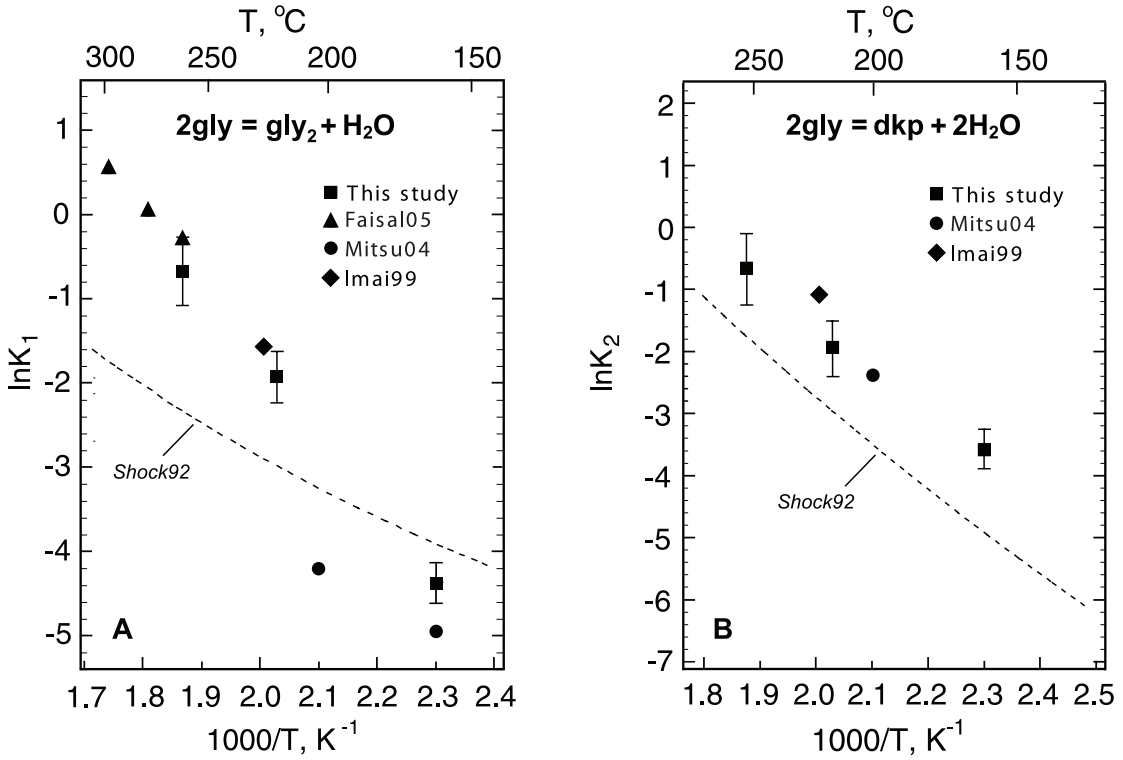

FIG. 3. Experimental and calculated van 't Hoff plots for peptide synthesis equilibria. Measured equilibrium constants $\ln K_1$ and $\ln K_2$ and computed van 't Hoff isochores using SUPCRT92 (Johnson *et al*., 1992) as a function of reciprocal temperature for (**A**) diglycine and (**B**) diketopiperazine synthesis from glycine at 200bar. Standard state thermodynamic properties and equation of state parameters used to calculate values for $\ln K_1$ and $\ln K_2$ (black dashed lines) are taken from Shock (1992). Values of $\ln K_1$ and $\ln K_2$ obtained from hydrothermal experiments are Imai99, Imai *et al*. (1999); Faisal05, Faisal *et al*. (2005); and Mitsu04, Mitsuzawa and Yukawa (2004).

The observed correlation between increasing temperature and exergonic shift of glycine-oligoglycine equilibria (Eq. 1) provides the basis for testing the hypothesis that hydrothermal systems on early Earth would have supported the formation of peptides. Experimental and calculated values of the natural logarithm of the equilibrium constant ($\ln K = -\Delta G_r^0 / RT$, see Eq. 3) for the formation of diglycine ($\ln K_1$) and diketopiperazine ($\ln K_2$) from glycine are shown as van 't Hoff isochore plots in Fig. 3 as a function of reciprocal temperature. From Fig. 3A it can be seen that our experimental values for $\ln K_1$ increase from -4.44 (± 0.25), through -1.93 (± 0.32) to -0.65 (± 0.43) at 160, 220, and 260°C, respectively, which suggests that the thermodynamic stability of diglycine relative to its hydrolysis product glycine increases with increasing temperature. Similarly, values for $\ln K_2$ are shifted toward more positive values with increasing temperature. Figure 3B demonstrates that the equilibrium constant for the cyclization reaction is shifted from -3.58 (± 0.31) through -1.95 (± 0.46) to -0.67 (± 0.56) for experiments at 160, 220, and 260°C, respectively, which suggests that the temperature increase corresponds to an increased thermodynamic stability of diketopiperazine relative to glycine. Interestingly, earlier work by Imai *et al*. (1999) and the more recent study by Faisal *et al*. (2005) demonstrated that, during its cycling in a hydrothermal flow-through reactor, glycine enters into a relatively rapid equilibrium with diglycine and diketopiperazine (see Fig. 3A, 3B). As can be seen from Fig. 3A and 3B, values for $\ln K_1$ and $\ln K_2$ obtained at 225°C by Imai *et al*. (1999) agree well with our results, though results by Imai *et al*. (1999) were obtained with quite different experimental techniques. Similarly, results for $\ln K_1$ obtained from 260°C to 300°C by Faisal *et al*. (2005) are in excellent agreement with our results [for example, the difference between our results for $\ln K_1$ and those reported by Faisal *et al*. (2005) at 260°C is 1.9 kJ $\cdot$ mol^{-1}; see Fig. 3A]. The situation is somewhat different for the results by Mitsuzawa and Yukawa (2004); while our values for $\ln K_1$ and $\ln K_2$ agree well with results from Imai's flow-through experiments and those by Faisal *et al*. (2005), values for $\ln K_1$ are significantly higher than those reported by Mitsuzawa and Yukawa (2004). Upon inspection of time courses of diglycine, generated in experiments from starting glycine (Mitsuzawa and Yukawa, 2004), it appears that values of $\ln K_1$ are likely to have been obtained under non–steady state reaction conditions and, in consequence, are likely to be underestimated. However, the rapid and facile formation of peptides from glycine in our experiments as well as in those by Imai *et al.* (1999) and Faisal *et al*. (2005) indicate that in natural hydrothermal environments, where amino acids have been demonstrated to form from simple organics and mineral assemblages (Hafenbradl *et al*., 1995), substantial quantities of these oligomers will form.

Prompted by these results, we calculated high-temperature and high-pressure standard state thermodynamic properties of aqueous glycine, diglycine, and diketopiperazine

via the HKF model for aqueous nonelectrolytes with the data previously reported by Shock (1992). Calculations were performed as follows: values for the equilibrium constants $\ln K_1$ and $\ln K_2$ were determined with use of HKF parameters for glycine, diglycine, and diketopiperazine, as published by Shock (1992). Results thereof are shown as equilibrium constants $\ln K_1$ and $\ln K_2$ in Fig. 3 (dashed lines, Fig. 3A, 3B). All calculations were performed via standard molal Gibbs energies, enthalpies, and third-law entropies for aqueous glycine reported by Wagman *et al*. (1982) and for diglycine and diketopiperazine from Shock (1992), together with the SUCPRT92 software package (Johnson *et al*., 1992). As may be seen from Fig. 3A, calculated equilibrium constants $\ln K_1$ (dashed line) at 220 and 260°C and at 200 bar are −3.02 and −2.41, respectively, and are offset by around 4.5 kJ · mol^{-1} and 7.8 kJ · mol^{-1} to lower values at 220 and 260°C, respectively, compared to our experimental values of $\ln K_1$ (see Fig. 3A). It is interesting to note that this difference is reduced to around 1.7 kJ · mol^{-1} at 160°C, a temperature at which HKF parameters for diglycine are more tightly constrained by experimental heat capacities and volumes. Calculated and experimental values of $\ln K_2$ (Fig. 3B, black dashed line) are in closer agreement than those for $\ln K_1$, with differences of 4.9 kJ · mol^{-1}, 3.9 kJ · mol^{-1}, and 4.6 kJ · mol^{-1} at 160, 220, and 260°C, respectively, relative to our experimental data. Finally, we emphasize that the similar slopes between our experimental and calculated (Shock, 1992) values of $\ln K_2$ shown in Fig. 3B suggest that the relative values of HKF parameters and enthalpy of formation of glycine and diketopiperazine reported by Shock (1992) are in fact good; however, the standard molal Gibbs energy of formation of diketopiperazine needs to be stabilized by approximately 4–5 kJ · mol^{-1} relative to 2 moles of glycine. In contrast, the relative values of HKF parameters reported by Shock (1992) for glycine and diglycine yield values of of $\ln K_1$, which do not match our experimental results and, when evaluated in terms of Fig. 3B, suggest that HKF parameters for diglycine need significant modification.

5. Conclusions

The results discussed here point to a thermochemical favor for amino acid oligomerization over peptide hydrolysis in hydrothermal solutions. The high-temperature formation of peptides from non-activated amino acids is a key step for the origin of life, as it would promote the capability to overcome the thermodynamic threshold imposed on the system during the initial phase of peptide elongation (Martin, 1998, 2001). Matsuno and coworkers showed that flow-through hydrothermal settings can facilitate peptide formation and elongation; however, any accumulation of prebiotic peptides would require a robust concentration mechanism (Baaske *et al*., 2007) as well as a significant thermodynamic driving force (Shock, 1992). A promising setting for the fast and thermodynamically favorable emergence of larger peptides and proteins would have been a natural hydrothermal flow-through system in which product peptides are continuously and rapidly shuttled between a high-temperature zone (*e.g.*, 250–370°C) and more moderate temperatures (<120°C) at which amino acids and peptide bonds remain stable over geological time periods. Results from this study support the hypothesis that hydrothermal systems on early Earth provided a suitable setting for the emergence of biomolecules and the origin of life.

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Abbreviation

HKF, Helgeson-Kirkham-Flowers.

7. References

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