Viva Origino 33 (2005) 41－172

S5-2

THE STABILITY OF NUCLEOBASES AND NUCLEOSIDES IN HYDROTHERMAL SOLUTIONS TO 220°C: AN *IN SITU* UV-VIS SPECTROSCOPIC STUDY

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Nucleobases are attached to the DNA backbone via the glycosidic linkage which undergoes spontaneous hydrolysis at 25°C.[1] Such hydrolysis reactions are responsible for endogenous DNA damage, mutation[2] and are regarded as a thermodynamic obstacle to the aqueous condensation route in prebiotic synthesis[3]. However, recent flow-through experiments on the stability of the glycosidic linkage in adenosine[4,5] point to a thermodynamic favour for nucleoside synthesis in hydrothermal environments. Prompted by these findings and recent reports on the kinetics of dinucleoside hydrolysis at elevated temperatures[6] we are currently undertaking a systematic study of selected nucleobases and nucleosides in hydrothermal media. Experiments were conducted in a Varian Cary 4E uv-vis spectrophotometer containing a high temperature high pressure gold-lined optical cell to minimize reactor wall effects. For every experimental run, nucleobase or nucleoside stock solutions ($\sim 10^{-5}$m) were pumped into the preheated cell and absorption spectra collected in batch-flow mode for time periods up to 6 hours. A preliminary analysis of the adenosine nucleoside absorption spectra at temperature of 140°C, 180°C and 220°C demonstrates (1) the establishment of a steady-state between the nucleoside and product nucleobase and ribose for each temperature, (2) a hyperchromic change in the double peak in the band around 210nm with respect to temperature and a reverse temperature dependence for the absorption band at 260nm for experiments at 220°C due to a n->π transition[7] and (3) a red shift in wavelength by around 5nm for runs at 140°C, 180°C and 220°C following the attainment of steady-state. The observation of a high temperature steady-state between nucleoside, nucleobase and ribose is of interest and will await further examination from both uv-vis spectroscopic and flexible gold bag studies. Knowledge of nucleoside hydrolysis as well as nucleobase decomposition rates and selected equilibrium constants at elevated temperatures is important to our understanding of organic synthesis in hydrothermal environments.

(1) Lindahl, T. (1993), *Nature*, **362**, 709
(2) Marnett, L.J. & Plastaras, J.P. (2001), *Trends in Genetics*, **17**, 219
(3) Boerio-Goates, J., Francis, M.R., Goldberg, R.N., da Silva, M.A.V. & Tewari, Y.B (2001) *J.Chem. Thermodynamics*, **33**, 929
(4) Ogasawara, H., Yoshida, A., Imai, E., Honda, H. , Hatori K., and Matsuno K. (2000) *Orig. Life Evol. Biosph.*, **30**, 519
(5) Ozawa, K., Nemoto, A., Imai, E., Honda, H., Hatori, K. and Matsuno, K. (2003) *Orig. Life Evol. Biosph.*, **34**, 465
(6) Kawamura, K. (2003) *Biochim. Biophys. Acta*, **1620**, 199
(7) Rich, A. & Kasha, M. (1960) *J.Am. Chem.Soc.*, **82**, 6197