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Effects of borate on the reaction between glyceraldehyde and glycoraldehyde

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Ribose is an essential component of RNA, and its formation in the prebiotic Earth is important to promote chemical evolution for origin of life. For the abiotic ribose formation, the formose reaction has been investigated by previous researchers [e.g., 1]. The formose reaction produces carbohydrates by series of polymerization of formaldehyde with catalytic base [2]. The carbohydrates produced in this reaction contain pentoses (ribose, arabinose, xylose, and lyxose). One of the problems is that these carbohydrates are highly reactive in alkaline solutions. Therefore, pentoses are rapidly decomposed. Recently, researchers proposed that ribose is stabilized by the complexation with borate and silicate [3, 4]. Ricard et al., (2004) offered the experimental data indicating the increased stability of the total amount of pentoses by the complexation with borate. However, there has been no clear evidence as to which pentoses are stabilized by effects of borate. Because the formose reaction produces variety of carbohydrates, it is difficult to perform quantitative analysis of each product. In particular, quantitative analysis of ribose needs chromatographic separation accompanied with mass spectrometry analysis. However, a previous analytical method for each pentose needed derivatization. In the present study, we report the qualitative analytical method for ribose in the mixture of pentoses without derivatization. Then, we analyzed ribose in the products of a simplified formose reaction in the presence of borate.

New analytical method for pentoses and pentose-borate complex was developed using a liquid chromatograph (2695 separation module; Waters Co.) connected to a tandem mass spectrometer (Quatromicro API; Waters Co.). Several ligand exchange columns and eluents were tested in order to identify the suitable combination to separate pentoses and pentose-borate complexes. As a result, pentoses were separated using the ligand exchange columns with a function of zinc coordination. The ligand exchange columns with a function of sodium coordination retained pentose-borate complexes. Using these analytical methods, we performed experiments to examine borate effects to stabilize individual pentose (experiment 1) and products by the simplified formose reaction under borate presence (experiment 2). In the experiment 1, decomposition rates of individual pentose were investigated in an alkaline solution. Experiments were performed either with or without sodium borate. The results indicate that the presence of borate affected differently on the stability of individual pentose. The decomposition rates of ribose and arabinose were decreased significantly in borate solution, although decomposition rates of xylose and lyxose were not affected by borate.

In the experiments 2, glyceraldehyde and glycolaldehyde was reacted in base with or without sodium borate. Formation of pentoses including ribose was confirmed and the yields of all pentoses became maximum within 5 minutes. After 5 min, the yields of pentoses decreased, although the yields of some pentoses experiments with borate became higher than those without borate. This result indicates that effects of borate differ depending on individual pentoses. In both experiments, the yields of ribose increased by the addition of borate. Pre-biotic ribose was most likely formed and stabilized under borate-rich Hadean oceans, which was also supported by finding of borate minerals in the early Archean sedimentary rocks.

References

[1] Butlerow, A., C. R. Acad. Sci. 53, 145?147 (1861). [2] Decker, P. et al., J. Chromatogra. 244, 281-291 (1982). [3] Ricardo, A. Carrigan, M. A.; Olcott, A. N., Benner, S. A., Science 303, 196 (2004). [4] Lambert, J. B., Gurusamy-Thangvelu, S. A., Ma, K., Science 327, 984?986 (2010).