

Farewell to a Friend

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Let's have a beer! At the European Summer School “Chemical evolution and the Origin of Life” organised by Alan Schwartz in 1983 in Stevensbeek, The Netherlands, the students were debating with three teachers, Jim, Alan and myself. Since our contribution, Jim and I, was apparently unneeded, I proposed to Jim to have a beer instead, loudly enough to release a big laugh from the audience. This anecdote reflects the friendly spirit shared by three prebiotic chemists tackling clays, nucleic acids and peptides, respectively.

Undoubtedly, Jim illuminated the prebiotic world of clay, paving the route to the RNA world (Ferris 2005, 2006; Huang and Ferris 2007). The key role of clay minerals in the origin of life was first suggested by Bernal (1949). The advantageous features of clays according to Bernal were (i) their ordered arrangement, (ii) their large adsorption capacity, (iii) their shielding against sunlight UV, (iv) their ability to concentrate organic chemicals and (v) their ability to serve as polymerization templates.

One of the successful applications of Bernal's proposal was contributed by Jim, when he showed that oligomers containing 6–14 monomer units are formed when RNA-like monomers ImpA (Fig. 1), activated on the phosphate with an imidazole group, condense in the presence of montmorillonite (Ferris and Ertem 1993).

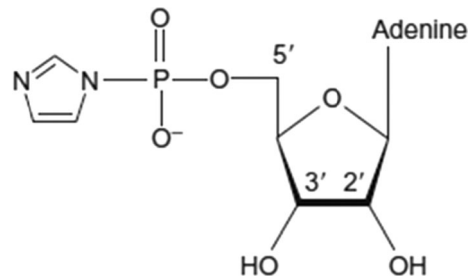
The formation of oligomers was generalized to the other nucleotide bases cytosine, guanine, inosine and uracil. Catalysis has the potential for limiting the number of isomers formed. For example, the natural 3', 5'-linked phosphodiester bond is favoured in the reaction of purine nucleotides on montmorillonite. The 2', 5'-linkage is favoured in the absence of catalysis. Analysis of the dimers formed in the reaction of mixtures of two or more activated nucleotides demonstrated strong sequence selectivity of the dimers formed (Ertem and Ferris 2000). The 5'-purine-pyrimidine sequence is favoured over the 5'-pyrimidine-purine sequence at the end of the polymer chain by a factor of about 20. In addition, five 5'-sequences (A-C, A-U, G-C,

Dedicated to the memory of Jim Ferris

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Fig. 1 RNA-like activated monomer ImpA with the 2', 3' and 5' positions for the phosphodiester linkages



A-A and GA) are formed in significantly larger amounts (73% total yield) than the 11 others in the reaction of mixtures of the four activated monomers of the nucleotides A, C, G and U.

The formation of short RNA-like oligomers with montmorillonite as catalyst was a possible first step in the formation of the RNA needed for the initiation of the RNA world. In a second step, Jim showed that it is possible to generate longer RNA by elongation of short oligomers (Fig. 2) using the 'feeding' protocol (Ferris et al. 1996; Ferris 2002).

The decanucleotide (pdA)₉pA bound to Na-montmorillonite was fed with ImpA, and the reaction mixture was allowed to stand for 1 day at 25 °C. The dispersion was then centrifuged to separate the aqueous phase from the montmorillonite. Fresh ImpA solution was added to the montmorillonite-oligomer complex, and the reaction was allowed to proceed for another day. Poly adenylates containing more than 20-mers were formed after feeding twice with ImpA, with the main products being 11–14 mers. Polynucleotides containing more than 50-mers were formed after 14 feedings, with the principal oligomeric products containing 20–40 monomer units. Twenty-five to thirty mers were obtained with the corresponding uridine-activated monomer (Ferris 2002).

Quite naturally, Jim came to address the intriguing question of homochirality and showed that montmorillonite facilitates homochiral selection, producing chirally pure oligomers of significant length at far higher abundances than expected by chance association (Joshi et al. 2011, 2013).

Jim was also interested in clay-mediated polymerisation of amino acids. It was known that the activation of amino acids using the condensing agent carbonyl diimidazole (Fig. 3) proceeds via the intermediary formation of an N-carboxyanhydride (Ehler and Orgel 1976; Brack 1987).

Glutamic acid was subjected to the feeding protocol using carbonyl di-imidazole. Illite was incubated with the amino acid and carbonyl di-imidazole until short oligomers were formed. The solid was separated by centrifugation, and fresh monomer and activating agent were added. The process was repeated as often as necessary for the production of oligomers of lengths of 40 or more. In the absence of illite, oligomers up to the 10-

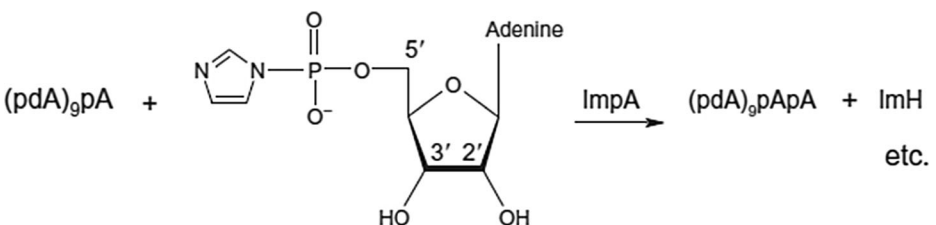


Fig. 2 Elongation of a decanucleotide by reaction with ImpA

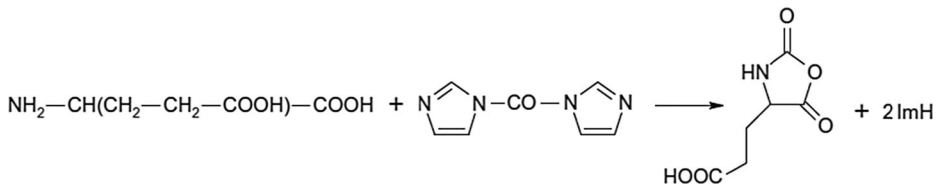


Fig. 3 Formation of the N-carboxyanhydride of glutamic acid with carbonyl diimidazole

mer were detected but the majority of the products were shorter than the 5-mer. In the presence of illite, the shorter oligomers remained in the supernatant while the longer oligomers adsorbed to the illite. After 50 feedings, oligomers up to at least the 55-mer were detected, the bulk of the adsorbed product being in the 30–50 size range (Ferris et al. 1996; Hill et al. 1998).

Finally, a nice tribute to Jim's work has been published by Gözen Ertem (Ertem 2004). For me, it was a great privilege to co-author Jim's two contributions to the Encyclopedia of Life Support Systems, an initiative launched by UNESCO (Brack and Ferris 2001a, b).



Jim and Susan at the ISSOL meeting in Florence, Italy, August 2008.

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