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ADENINE PHOSPHORAMIDE AS A POSSIBLE PRECURSOR OF ATP

BY

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ABSTRACT

Adenine phosphoramide as a possible precursor of ATP. - The acid-opened phosphoramide bond of adenine triphosphate can possibly be bridged by amphihydroxylated ribose precursors and thereby evolve into adenosine triphosphate.

Key-words: phosphoramide, adenine, triphosphate, ribose, adenosine.

INTRODUCTION

"The prebiotic synthesis of nucleotides remains an unsolved challenge" (BRACK, 1998), because of the scarcity of ribose produced among a larger number of other sugars (SHAPIRO, 1988; JOYCE, 1989; JOYCE & ORGEL, 1999; LAHAV, 1999). The complex biotic synthesis of the "modern energy currency" adenosine triphosphate (ATP) which involves ribonucleotide formation, would therefore have been impeded in prebiotic conditions. In 1965, FRITZ LIPMANN, the founder of bioenergetics, had already proposed that simple condensed phosphates such as pyrophosphate (PPi), triphosphate or polyphosphates from primitive environmental sources might have been the forerunners of ATP, as further enforced by BALTSCHEFFSKY (1993) with his prebiotic "PPi world".

However, consideration of the chemical evolution from a bottom-to-top point of view has led to predict a progressive arisal of affinity of the available phosphates for the early synthesized nucleobase adenine (5 HCN, ORÓ, 1960), in anticipation of their linking by ribose precursors ($C_2 + C_3$) produced by the well-known formose reaction (see SCHWARTZ, 1998).

Our finding of a prebiotic-like direct phosphoramidic (P~N) bonding (TURIAN *et al.* 1999; TURIAN & RIVARA-MINTEN, 2001), bypassing the double bonding – phosphoesterasic and glycosylic – of ribose, has recently suggested a stepwise insertion of ribose precursors between acid-induced opened P~N bonds of pre-RNA (TURIAN, 2001a) as also proposed below for the transition from sugarless adenine triphosphate to the adenosine triphosphate of ATP.

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MODEL

It rests on the contrast between the robustness of our nucleobase P~N bondings at high pH (~8 TURIAN *et al.*, 1999), also known for imidazole (LOHRMANN & ORGEL, 1973), and other phosphoramides (CORBRIDGE, 1978) and the lability of their P~N bonds in acidic pH (< 4) conditions. This opens the interesting possibility to fill the gap — opened by acidification to pH 4-2 — between the nucleobase and the first phosphate group by ribosylating compounds (Fig. 1).

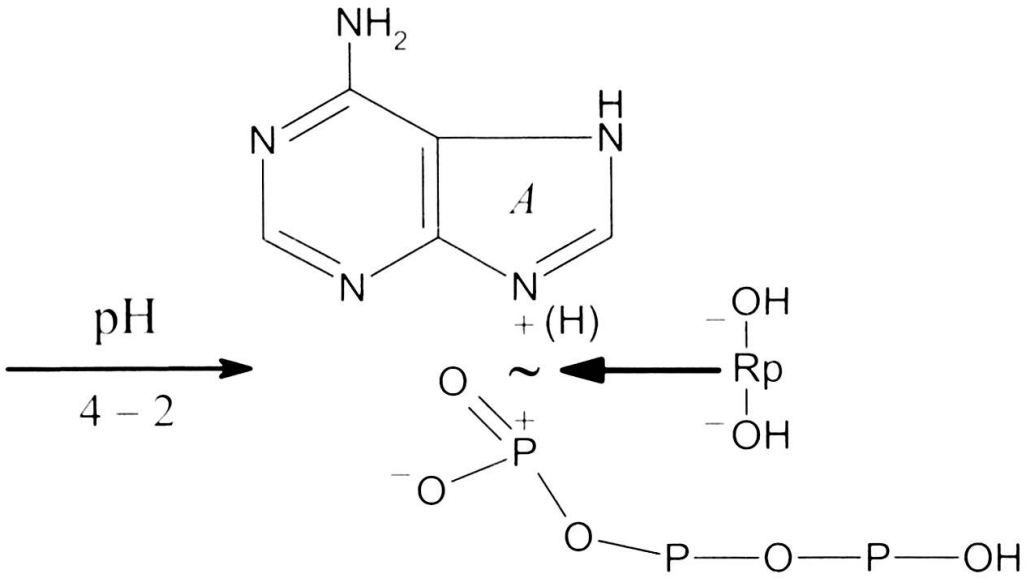

FIG. 1. Final step in the prebiotic origin of adenosine triphosphate implies acid-opening (pH < 4) P~N of the bonding between adenine *(A)* and triphosphate and further bridging by amphihydroxylated ribose precursors (Rp). For the initial steps of P~N bonding on "low tautomerized" adenine, see Fig.1 in TURIAN (2001a,b).

This model therefore involves the median, symmetric insertion of the hydroxylated precursors of ribose between the two acid-opened poles ^{+}N and P^{+} of the adenine phosphoramide. These $C_1 \rightarrow C_2 + C_3$ compounds could secondarily condense into the pentose C_5 according to the following symmetric-sequence of ribosylation:

Adenosine

A – [glycolaldehyde - glyceraldehyde] – 3P
$C_2 + C_3$

D-ribose

Of evolutive significance, it should be emphasized that the two high-energy bonds generated by a gradient of protons in the biotic synthesis of ATP from AMP were automatically present in prebiotic adenine triphosphate which incorporates the two terminal P anhydride bonds of its cyclic triphosphate precursor (see Fig. 1).

CONCLUSION

To the question "How to make a nucleotide?", be it ATP or a monomer of RNA, it has been theoretically and experimentally answered by *asymmetric* processes, either covalent glycosylation of the nucleobases on ribose (poly)phosphate (KORNBERG, 1954-55, PITSCH *et al.*, 1995; MOJZSIS *et al.*, 1999) or phosphorylation by trimetaphosphate of first heat-produced ribonucleosides, as pioneered by LOHRMANN (1977) and ETAIX & ORGEL, (1978). Recently, ZUBAY & MUI (2001) have favored the first alternative according to which ribose was probably phosphorylated prior to becoming linked to the nucleobase in such a way that "the nucleoside formation step was bypassed in favor of nucleotide formation".

However, in the early prebiotic conditions, when ribose was hardly available, nucleotide synthesis such as that of ATP, would necessarily have occurred in a two-step process modellized above: first by the bypass of a direct phosphoramide bonding of adenine and phosphate groups, secondarily, by *symmetric* insertion of ribose precursors.

RÉSUMÉ

Adénine phosphoramide comme possible précurseur de l'ATP ? - La liaison phosphoramide de l'adénine triphosphate, ouverte par acidification, pourrait être pontée par des précurseurs amphihydroxylés du ribose qui la ferait évoluer en adénosine triphosphate.

Mots-clés: phosphoramide, adénine, triphosphate, ribose, adénosine.

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