



Note

Stabilization of ribofuranose by a mineral surface



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ABSTRACT

The existence of the ribose moiety in biomolecules poses two problems for prebiotic chemistry. First, the exclusive presence of the furanose isomer in RNA has to be accounted for since furanose is a minor form in solution and does not exist in crystals. Second, all D-ribose polymorphs are unstable in aqueous medium so that a stabilization mechanism has to be invoked. We observed that the adsorption on mineral surfaces as amorphous silica protects the sugar from degradation processes. Moreover, this silica surface, used as realistic chert model, is able to increase significantly the proportion of ribofuranose compared to ribopyranose forms. The interaction between surface and sugar was analyzed by ¹³C NMR. Our results show a very significant chemical and thermal stabilization of the adsorbed sugar by a silica surface and an almost twofold increase of ribofuranose compared to ribose in solution.

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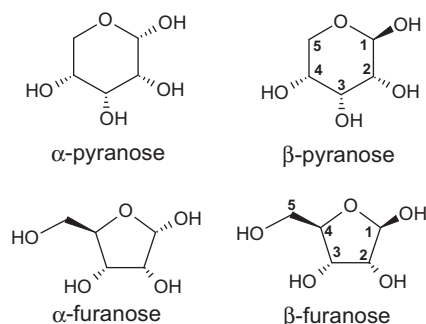
Ribose, a simple sugar with the formula C₅H₁₀O₅, is a major component of the nucleotides that form RNA. In the context of prebiotic chemistry, its synthesis, stabilization, and chemical reactivity are particularly interesting, especially to assess the 'RNA World' hypothesis.¹

In this scenario, autocatalytic and informational RNA molecules are the first complex biopolymers to have emerged and provide a missing link between small molecules and living organisms. Even though interesting chemical pathways leading to the synthesis of nucleotides have been proposed that need not go through the free sugar,² it remains legitimate to wonder how the sugar component could have arisen. It could have been synthesized prebiotically by the formose reaction,³ based on the polymerization of formaldehyde and first evidenced by Butlerow in 1861, although as a rather minor product of this reaction.⁴ It is not enough to form ribose however, since a problem of isomer selection is encountered. Ribose presents four polymorphs, two with a pyranose and two with a furanose ring (scheme 1). Only the β-furanose form is used in RNA molecules. Moreover, D-ribose is unstable in solution. For example, at pH 9 and 60 °C, its half life is about 50 h; in more physiological conditions, at pH 7 and 37 °C, it should be around 500 h if one extrapolates from the data of Miller and co-workers.⁵ In the

solid state, the furanose form does not exist.⁶ Thus, two questions need to be answered: (i) how have the ribofuranose forms emerged and been selected to form RNA molecules; (ii) how has this sugar been stabilized in solution? A tentative answer to the second question is that borate complexes could have acted as ribose stabilizing agent.^{3,7} At least two studies have claimed that silicates in solution can also stabilize ribose during the formose reaction.⁸ Although this has not been observed in another experimental investigation,⁹ theoretical studies have confirmed that the ribose–silicate 2:1 complex is more stable than other pentose and hexose complexes, a concept experimentally verified by Lambert et al., and constituting a first example of selectivity of interaction between mineral centers and sugars.^{8a} Furthermore, theoretical results have also shown that silicate complexes should be formed exclusively with the furanose form because in the latter form, the HO–C–C–OH dihedral angle is sufficiently small to allow the formation of a planar five-membered ring^{8a} including the silicon atom, so that the silicate scenario could also help answer our question. (i) Since interaction with silicate is possible in solution, a third question can be asked: (iii) could silica or silicate surfaces have played a role in the emergence and stabilization of ribose and more specifically of ribofuranose? The influence of mineral surfaces on the formose reaction has been previously addressed.¹⁰ Montmorillonite, calcite, hydroxyapatite and alumina seem to promote the formation, in minor proportions, of unbranched aldoses. In these studies, no selectivity of condensation for specific ribose polymorphs was

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Scheme 1. Ribose polymorphs.

observed. Of course, chemical analysis of minor products in a complex mixture is difficult and it seems necessary as a first step to analyze more precisely the interaction between monosaccharides and different mineral surfaces. In this respect, a few studies have analyzed the adsorption of ribose and nucleoside on clay mineral surfaces.¹¹ For example, Aisawa et al.^{11a} have adsorbed ribose on anionic clay minerals (LDH). The intercalation of ribose was observed in the interlayer space of clay, and it was claimed that the furanose form predominated, but the possible stabilization toward degradation was not discussed.

The present work focused on the interaction of ribose with an amorphous silica (SiO_2) with a high surface area ($380 \text{ m}^2/\text{g}$), Aerosil 380, and its relation to isomer selectivity and stability. Silica represents a possible model of mineral phases existing on the primitive earth such as cherts (microcrystalline silica-containing sedimentary rocks), and in addition organic species supported on it are easy to characterize.¹² We indeed observed that ribose confinement by adsorption on this surface significantly shifts the isomerization equilibrium to furanose and in addition stabilizes the adsorbed sugar against degradation.

1. Experimental

Ribose was provided by Sigma. Aerosil 380 (SiO_2) was provided by Evonik. It is a non-porous fumed silica with a BET surface area of $380 \text{ m}^2/\text{g}$.

1.1. Adsorption procedures

Ribose adsorption was carried out by impregnation or by selective adsorption methods. In the impregnation procedure, 300 mg of silica was wetted with a ribose solution (3.3 mL). The obtained paste was stirred at room temperature for 3 h and dried at 70°C in an oven. In the selective adsorption procedure, 300 mg of silica was dispersed in 25 mM ribose for 3 h at room temperature and stored at 70°C for 150 h at pH 9. The solid phase was separated from the liquid phase by centrifugation, and then dried at 30°C .

1.2. Analytical techniques

- ^{13}C NMR: HP-DEC sequences (proton high power decoupling) were recorded at room temperature with a Bruker Avance 300 spectrometer with a field of 11.8 T equipped with a 4 mm MAS probe with a spinning rate of 10 kHz. The pulse angle was 30° , decoupling was applied at 50 KHz, and the recycle time was 10 s. CP-MAS sequences were recorded at room temperature on the same apparatus. The contact time was $1000 \mu\text{s}$ (other values were tested as well, see [Supporting information](#)) The recycle time was 1 s for adsorbed ribose and 300 s for bulk ribose.

- TGA of the samples was carried out on a TA Instruments Waters LLC, with a SDT Q600 analyzer, using a heating rate $\tau = 5^\circ\text{C}/\text{min}$ under dry air flow ($100 \text{ mL}/\text{min}$).

2. Results and discussion

TGA (thermogravimetric analysis) of bulk D-ribose shows an endothermic event without weight change at 90°C , due to ribose melting,¹³ followed by four weight-loss events (195°C , about 20%, endothermic; 280°C , weakly exothermic, and 320°C , strongly exothermic, 51%; and 510°C , around 29%, strongly exothermic and resulting in complete combustion; [Fig. 1](#) and [SI-Fig. 1](#)). Here we do not intend to discuss these events in detail but to use them as a fingerprint. The endothermic weight loss at the low temperature of 195°C could suggest ribose polymerization with water elimination, but complete linear polymerization would result in a 13% weight loss while the observed value is almost twice higher.

Since we were interested in ribose stability, we also left a 60 mM ribose solution to dry in an oven at 70°C (i.e., in the same conditions as used later for the preparation of ribose/silica, but without addition of any silica). The final product was a brown gel. This material had clearly undergone significant chemical modifications with respect to the starting ribose. Thus, its TG (see [Supporting information](#)) was totally different from that of ribose, and in particular did not show any melting transition at 95°C , indicating that the drying process had caused significant modifications in the ribose structure and confirming the well-known thermal instability of the latter molecule. The brown gel obtained from drying of the ribose solution at 70°C shows significant modifications in its ^{13}C solid-state NMR spectrum (see below), indicative of ribose degradation. New peaks appear at 107 ppm and below 100 ppm, corresponding to new carbon environments, and carbonyl environments appear at 180 ppm, probably corresponding to the linear form of the ribose.

Ribose was then adsorbed onto silica (with a 10 weight% loading, see [Section 1](#)), submitted to oven drying at 70°C , and its thermal reactivity investigated. Between 20°C and 110°C , a large amount of water was eliminated, indicating that the apparently dry sample actually contained no less than 32% weakly held water. Two broad thermal events were observed at higher temperatures: the first one with a $T_{\text{max}} = 185^\circ\text{C}$ is almost athermic and corre-

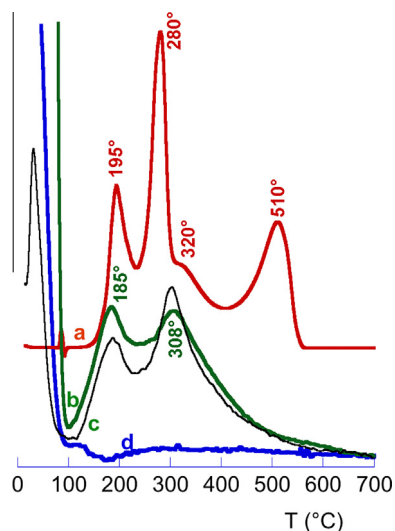


Figure 1. DTG (derivative of thermogravimetric signal) of bulk D-ribose (a), 10 weight% D-ribose on silica dried under air (b), the same dried under vacuum (c), the dried silica support (blank, d).

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