

# Putative mechanism of the sugar formation on prebiotic Earth initiated by UV-radiation

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## Abstract

UV-irradiation of neutral aqueous formaldehyde solutions leads to the formation of a number of products. CO, CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub> are the main products detected in the gas phase over the solutions. In the liquid phase, glycolaldehyde and glyceraldehyde are among the products with the maximum yields of 4.2% and 0.18%, respectively. These aldehydes are shown to be the most active initiators of the formose reaction in the dark to synthesize monosaccharides from formaldehyde. The amounts of the photolytically formed initiators are sufficient for the initiating the formose reaction.

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## 1. Introduction

Monosaccharides, or carbohydrates, along with proteins and fats create the basis of living matter with the estimated mass nearly  $2.5 \times 10^{18}$  g of carbon on Earth. Monosaccharides constitute cellular membranes and participate in many processes occurring in living organisms. One of the most important carbohydrates is ribose, which is the key component of ribonucleic acids.

Could sugars be synthesized in macroquantities in the primordial world? One can expect that “yes”. A probable source of these compounds is the formose reaction discovered by the Russian chemist Butlerov as long ago as in 1861 (Khomenko et al., 1980):



The reaction represents the condensation of formaldehyde into higher carbohydrates in aqueous alkaline solutions in the presence of some metal cations, the alkaline-earth metals cations (in particular, Ca<sup>2+</sup> and Mg<sup>2+</sup>) being the most active. This is an autocatalytic reaction, which is initiated and accelerated only in the presence of carbohydrates (Khomenko et al., 1980).

Note that formaldehyde is detected in significant amounts in molecular clouds in space (Litvak, 1972). Undoubtedly, this compound was an important gaseous component of the circumsolar protoplanet disk. For this reason, formaldehyde could be captured during the planet formation and then dissolved in water of Protoearth. Calcium and magnesium, which are capable of creating an alkaline medium, are well-known most abundant elements of our planet. Thus, the basic conditions for the formose reaction and for the formation of monosaccharides in nature could be met. However, the initiation of the formose reaction needs a monosaccharide primer, at least a simple compound of this type. It has been a common opinion for long that the simplest of monosaccharides like glycolaldehyde (Fig. 1, 1) can be a product of

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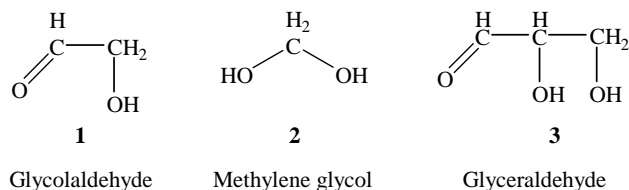
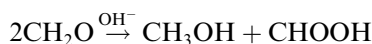


Fig. 1. Structural formulas of glycolaldehyde (1), methylene glycol (2), glyceraldehyde (3).

the formaldehyde dimerization under conditions identical to the conditions of the formose reaction (e.g. Harsch et al., 1983). However, such dimerization has been shown to be impossible, since only disproportionation of formaldehyde into methanol and formic acid by the Cannizzaro reaction takes place in the aqueous formaldehyde solutions in the absence of the monosaccharide primer (Socha et al., 1981):



Since glycolaldehyde is not only the simplest carbohydrate but also the most active initiator of the formose reaction (Uspenskaya et al., 1971), a question arises how the first molecules of glycolaldehyde could be formed as the formose reaction primer and, consequently, how the first monosaccharides could be formed.

There are alternative hypotheses of sugar formation on the “prebiological” Earth. In the system developed by Eschenmoser et al. (Müller et al., 1990) base-catalyzed aldol condensation of glycolaldehyde phosphate leads to mixture of the eight aldohexose-2,4,6-triphosphates. Phosphorylation of glycolaldehyde, in the case, results in the formation of less complex mixture than in classical formose reaction due to preventing of chain sugars formation. Besides aldol, condensation of glycolaldehyde was observed by Weber (1998) at ca. pH 5 in the presence of ammonia. Actually, these processes and formose reactions are the different variants of the same base-catalyzed reaction of aldol condensation between formaldehyde and sugars having  $\alpha$ -hydrogen including glycolaldehyde or between sugars themselves:



(where  $\text{R}^i = \text{C}_i\text{H}_{2i+1}\text{O}_i$ ,  $i = 0, 1, 2, \dots$ ).

In that case the question how glycolaldehyde has appeared under “prebiological” conditions follows the question whether the sugars formation has been possible as a result of one of these processes.

It is known that glycolaldehyde can be formed when formaldehyde frozen in vacuum (Hudson and Moore, 2004) or in matrix of inert gas at temperatures 10–100 K is exposed to radiation or UV-irradiation (Irie, 1989). The mentioned process was impossible indeed at high-temperature conditions of the Protoearth, when glycolaldehyde decomposes. It was discovered in the

beginning of the 20th century that the condensation of formaldehyde in aqueous solutions can be initiated by an UV-radiation by the sunlight or a mercury lamp. For example Baly (1924) observed the formation of a reductive mixture of monosaccharides in an UV-irradiated 40% formalin solution in the presence of  $\text{CaCO}_3$ ; the reported yield of monosaccharides was 8%. Shigemasa et al. (1977) reported the formation of 2-hydroxy-methylglycerol (yield 40%), pentaerythritol (yield 13%) and carbohydrates (yield 2–8%) in aqueous 8 M formaldehyde under irradiation of a mercury lamp. The reaction was conducted during several days in the presence of 0.6–1.2 M inorganic alkaline catalysts such as NaOH,  $\text{Na}_2\text{CO}_3$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$ . In the absence of a catalyst, a decrease in the concentration of formaldehyde exposed to the UV-irradiation was negligible. A more recent report (Schwartz and Graaf, 1993) also described a highly selective synthesis of pentaerythritol (yield 28%) in the 0.1 M aqueous formaldehyde solution under UV-radiation of a mercury lamp in the presence of 0.05 M  $\text{Na}_2\text{CO}_3$ . A high selectivity to glyceraldehyde and pentaerythritol was also reached by exposing formaldehyde solutions to  $\gamma$ -irradiation in the presence of 0.3 M inorganic bases (Irie, 1989).

However, the occurrence of the highly concentrated aqueous solutions of inorganic bases seems to be improbable under natural conditions of Protoearth. Besides, in aqueous solutions, formaldehyde exists in the hydrated form of methyleneglycol (Fig. 1, 2). The maximum of the single adsorption band of methyleneglycol is at approximately 200 nm, while all of the used alkaline catalysts absorb the UV-radiation at the wavelengths less than 240 nm. Hence, the mercury lamp radiation in the experiments under consideration seems to affect mostly not the substrate but the base catalyst, i.e. the  $\text{OH}^-$  ions, to cause the formation of hydroxyl radicals. This process is followed by the conventional thermal processes such as the acyloin condensation, aldol condensation and crossed-Cannizzaro reaction (Irie, 1989).

Thus, it is important to understand if the primer monosaccharide needed for the initiation of the autocatalytic synthesis of monosaccharides can be a product of photochemical reactions in neutral aqueous solutions. Our work is devoted to the investigation of products formed under the UV-irradiation at wavelength 193 nm of a neutral aqueous formaldehyde solution. The possibility of the initiation of the formose reaction in the presence of these products also was studied.

## 2. Experimental

### 2.1. Chemicals and solutions

Commercial reagents of chromotropic acid’s disodium salt (analytical purity grade),  $\text{H}_2\text{SO}_4$  (special

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