



## RADIOLYSIS OF AQUEOUS GLYCERALDEHYDE

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**Abstract.** *Chemical evolution encompasses the formation of organic molecules before the appearance of life. In this context, we study the radiolysis of glyceraldehyde, a key molecule for the formation of sugars and other compounds. The glyceraldehyde was very unstable under irradiation and formed many sugar-like products. The most important for chemical evolution are ethylene glycol and glycolaldehyde.*

**Key words:** *Glyceraldehyde, chemical evolution, gamma irradiation*

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### 1. ORIGIN OF LIFE

Several hypotheses have attempted to explain how life could emerge as a result of physicochemical interactions between molecules that probably existed on the early Earth. From the scientific point of view, there are two: first is the genetic approach, which proposes the gradual accumulation of organic compounds by chemical evolution processes, proposed independently by Alexander I. Oparin and John B. S. Haldane [1, 2]. On the other hand, the metabolic approach proposes the existence of a primary metabolism [3]. Either of these hypotheses requires the synthesis and preservation of organic material from simpler compounds [4].

The study of the origin of life has been divided into three main stages: chemical evolution, prebiological evolution, and biological evolution. This work is framed in the stage of chemical evolution.

Chemical evolution has been defined as the series of physical and chemical processes that lead to the abiotic formation of organic compounds of biological importance. Such processes are simulated under conditions that likely existed on early Earth [4] with the objective of explaining the mechanisms by which organic molecules were formed and increased their complexity.

In chemical evolution studies, equally important as the synthesis of biologically important compounds is their ability to prevail in the environment; therefore, there must be a balance between the formation and the destruction of these molecules for them to be available for further use.

### 2. ALDOSES: BIOLOGICAL IMPORTANCE AND RELEVANCE IN CHEMICAL EVOLUTION

Sugars of the aldose type are of significant biochemical interest because of the number of metabolic roles they play in biological systems as structural or energy molecules. This group of molecules is also important in the context of chemical evolution. The synthesis and preservation of aldoses in prebiotic conditions is fundamental for their role in energetic functions and to the abiotic formation of nucleotides and nucleic acid components (i.e., RNA), which are compounds that could be proposed as the first self-replicating systems [5]. Glyceraldehyde is a molecule that contains both an aldehyde group and a hydroxyl group. It is a highly reactive molecule and it occurs in the biosphere [6]. In addition, this type of molecule could have formed in the ice of star-forming clouds -- and could be a potential source for the organic matter to the Earth [7]. According to Weber and Pizzarello [6] glyceraldehyde was probably present on the prebiotic Earth, since it has been synthesized under prebiotic conditions [6 and the references therein].

Existing sources of energy on the early Earth, which were useful for the abiotic synthesis of organic matter, are an essential part of chemical evolution because energy is responsible for initiating, promoting, and directing all physicochemical processes [4, 8]. Energy in the form of ionizing radiation was likely of great importance in chemical reactions that were conducted on the early Earth and in the interstellar space [8, 9, 10]. For these abiotic forms of synthesis, ionizing radiation may have had an important role because of

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its high efficiency in inducing the synthesis of organic compounds, its penetration into matter, and its relative abundance. There are two contributors: ionizing radiation from the Earth's crust for the presence of radionuclides and radiation from extraterrestrial sources such as cosmic rays or solar wind [8, 9, 10, 11]. Estimates of the energy inventory of the early Earth for the contribution of radioactivity are roughly equivalent to that provided by electric discharges [8]. In particular, the contribution of  $^{40}\text{K}$  is particularly important due to the fact that it delivers about 0.5 MeV at each decay, it is well dispersed in the oceans, its half-life is  $1.2 \times 10^9$  years, and its abundance on the primitive Earth was almost 10 times higher than at present [8, 9, 11, 12].

The primary objective of this work is focused on studying the stability of organic molecules of biological and prebiological importance under ionizing radiation fields. To this end we investigate the radiolysis of glyceraldehyde in aqueous solution, varying the adsorbed dose. Glyceraldehyde is considered the simplest triose. It is readily formed in prebiotic experiments simulating extraterrestrial ices [7] or in terrestrial conditions [6]. Its interaction with radiation may give rise to the formation of sugar-like products.

### 3. METHODOLOGY

#### 3.1 Preparation of samples:

Aqueous solutions of glyceraldehyde (Merck Co. USA) in concentrations from  $10^{-4}$  M to 0.1 M were prepared for analytical purposes. For irradiation 0.01 M aqueous solution samples, saturated with argon were prepared with triple-distilled water in sealed culture tubes. The glassware was treated according to the standard of radiation chemistry [13].

#### 3.2 Irradiation of samples

The irradiation was carried out using a high-intensity radiation source of cobalt-60 (Gammabeam 651PT) at ICN-UNAM. The samples were irradiated at room temperature (298 K) with a dose rate of 98 Gy/min and an interval of doses of 0 to 8.2 kGy.

#### 3.3 Analysis

The compounds were analyzed by chromatographic techniques, principally gas and liquid chromatography coupled with mass spectrometry. Another analysis was done through UV spectroscopy. The samples were analyzed immediately after irradiation.

### 4. RESULTS

Information about the radiation chemistry of ketones and aldehydes, both in aqueous solution and in the solid state, is scarce. In particular, the radiation-induced transformation of aldehydes is a complex problem. Elucidation of the entire mechanism may be unraveled only by conducting a detailed analysis of the transient intermediates, identifying the primary stable radiolysis products, and taking into account the

kinetics and yields of their formation [14]. These preliminary results show that glyceraldehyde is very unstable under irradiation in aqueous solutions. It formed a yet-unidentified compound that has a higher absorption in UV, accompanied by a hypochromic shift of the maximum of absorption to 245 nm (Fig. 1).

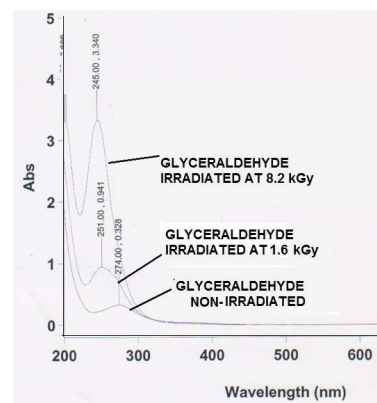


Figure 1. UV spectra for glyceraldehyde

This shift increased with the dose of irradiation. A possible explanation is that this maximum corresponds to malonaldehyde, a common product formed in the radiolysis of carbohydrates that absorbs at that wavelength [15]. Other identified products are ethylenglycol and glycolaldehyde (mw 60), which is the smallest sugar molecule identified in the interstellar space [16]. Other product identifications are currently under study. In the formose reaction, glycolaldehyde condenses with formaldehyde to form sugars and resulting tetroses.

In the case of aqueous solutions, the hydration of carbonyl group reaches equilibrium very rapidly, and the hydrated form also can be attacked by the water radiolysis products. The observed products can be explained by the secondary attack of water radiolytic products, many of which are formed in small amounts. The  $\cdot\text{OH}$  radical is a powerful oxidizing agent and is very reactive with aldehydes [14, 17]. Identification of some products after radiolysis by liquid chromatography-mass spectrometry, revealed that oxidation is one of the predominant transformations. This process yields oxidized products with an unchanged or a shorter carbon chain.

The pattern of hydroxyl radical reactions with a solute depends upon the chemical structure. ESR and other methods have shown that the most typical reaction of OH with polyhydroxyl compounds is the abstraction of hydrogen atoms bound to carbon according [14, 17-20]. Additionally, glyceraldehyde in aqueous solutions is in equilibrium with its hydrated form. Some possible pathways for the decomposition of glyceraldehyde, based in [17-20] in which water elimination reactions and detection of CO were detected are: (Fig. 2)

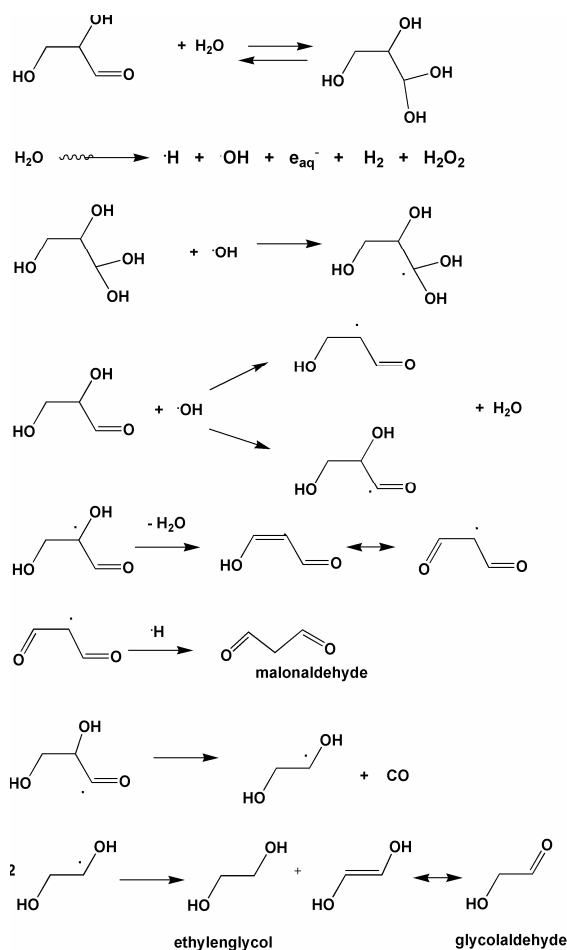


Figure 2. Possible mechanisms for the radiolysis of glyceraldehyde

## 5. REMARKS

Glyceraldehyde is an important molecule in chemical evolution studies. Radiolytic decomposition forms many compounds, some sugars-like products, so that decomposition may be a pathway for the formation of important sugars and other compounds related to bio-organic compounds under primitive Earth conditions. In particular, the formation of glycolaldehyde is important because this compound has been identified in the interstellar space and is an intermediate in the path to forming molecules that are more complex.

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