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Ionizing Radiation, an Instrument in Chemical Evolution Studies: Scope and Perspectives

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ABSTRACT

The study of synthesis and stability of molecules in different environments it's been part of chemistry evolution and origin of life studies for more than 70 years. Various kinds of ionizing radiation have been analyzed as possible sources of energy for the transformations undergone by the first organic molecules. Now experimental and computational simulation approaches continue with different groups of organic molecules, in search for more information that help us to understand and reconstruct somehow the mechanisms that toke place on early Earth and space. In that line, this paper presents first approach of keto acids stability to ionizing radiation, an interesting group of molecules involved in the Krebs cycle and glycolysis. Preliminary results obtained by HPLC/UV analysis of irradiating aqueous solutions of 5 keto acids ranging from 3 to 6 carbons with a ^{60}Co gamma ray source, using doses up to 53 kGy, show different stabilities and a general tendency of shifting the keto-enol equilibrium to the enol tautomer before decomposition.

1. Introduction

Space and early Earth are hypothetical scenarios with environmental conditions that represent a challenge for the survival of simple organic molecules and their evolution into more complex ones. Organic molecules diluted into vast oceans and the presence of high radiation fields of ionizing radiation sources, like radioisotopes and cosmic rays, with high penetration capacity, might have made specially complicated for these first organic molecules to survive and react with each other to evolve [1]. Experimentation in this field has been made with different kinds of ionizing radiation. First, due to its ubiquity and abundance, the relevance of UV light was evaluated and its capacity of synthesis and degradation of molecules was experimentally evidenced, including its possible implications in the development of homochirality. Other forms of ionizing radiation were considered, even when they were relatively scarce and sometimes more destructive (due to their higher energies), because they were found to be able to penetrate deeper into matter and lead reactions where others can't [2].

Studies in radiation chemistry can provide a deeper insight into chemical processes that may be important for origin of life, such as that related to some relatively labile compounds like keto acids, that are part of apparently ancient and critical metabolic processes [3]. To this end, we investigated the survival of keto acids exposed to a high radiation field in an aqueous solution. Keto acids are organic compounds that contain a carboxylic acid group and a ketone group (that stays in equilibrium with the hydrated form). Depending on structure, they can be typically alpha, beta and gamma keto acids. Keto acid and their derivatives are important compounds in biological systems. Alpha-keto acids are especially important in biology, as they are involved in the Krebs citric cycle and in glycolysis. Some other appear in a wide variety of anabolic pathways in metabolism, across living organisms, like the production of some alkaloids in plants, so, their synthesis and stability in environmental conditions is of paramount importance in chemical evolution [3,4].

Studies of their stability in primordial environments are scarce, especially those related to the stability in an aqueous medium at high temperatures or in the presence of high radiation fields. Compounds such as pyruvic acid, oxalacetic acid, citric acid, isocitric acid, alpha-ketoglutaric acid (all members of the citric acid cycle), and others have been just recently identified in extraterrestrial sources (in carbonaceous meteorites) and/or as low temperature (laboratory) reaction products of pyruvic acid [3,5,6], but

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up to now, the abiotic synthesis of these compounds has not been fully understood, and their synthesis is at least difficult in prebiotic chemistry. Considering these combinations of factors, the detailed study of these kinds of molecules seems to be a promising way to understand the role of each one and reconstruct somehow the mechanisms that toke place in the development of organic molecules that constituted life from the beginning.

2. Methodology

Aqueous solutions of 5 keto acids –pyruvic acid, oxalacetic acid, alpha-ketoglutaric acid, beta-ketoglutaric acid and 2-oxoadipic acid– were prepared in concentrations of 0.01 M and 0.001M at their natural pH values (6, 2, 3, 3 and 5, respectively). All were high purity standards from Sigma-Aldrich prepared in triple distilled water according to the techniques used in radiation chemistry [2]. The stability of these solutions was followed during 2 weeks using high-performance liquid chromatography (HPLC) coupled with a UV light detector at 210 nm. Two different chromatography columns were used for the analysis: an anion exclusion column (Alltech, 300 × 7.8 mm, 1.0 mL/min of H_2SO_4 0.0015 M) and a C-8 column (Halo C8, 100 × 2.1 mm, 0.5 mL/min of water/methanol, 80:20).

After that period, solution samples were irradiated in absence of oxygen (removed by saturating the solutions with argon) by exposing them to different doses of gamma radiation from a cobalt-60 gamma-ray source (Gammabeam 651 PT) at an average fixed dose rate (170 Gy/min). The dose interval was from 0 to 53 kGy. All glassware used was previously treated with nitrating mixture and triple distilled water, and finally dried in a furnace at 300°C, according to Draganic and Draganic protocol for removing organic matter [7]. Samples were analyzed after irradiation by HPLC/UV. The peak areas were used to calculate results. To start identifying the radiolysis products, standards of other acids were also injected: citric, glyceric, maleic, malic, malonic, glutaric, lactic, succinic and hydroxyglutaric acids.

3. Results and Conclusions

The stability analysis of aqueous solutions of the five selected keto acids reveled that the samples do not decomposes so easily in that conditions, so all the changes registered in the irradiated samples were effect of ionizing radiation. All five keto acids used in this research display the typical equilibrium between the keto-enol tautomers. Like for most of this kind of isomers, equilibrium favors the keto tautomer, except in the oxalacetic acid and the beta-ketoglutaric acid, which present a special structure that aloud the enol tautomer stabilizes by resonance with a carboxylic group and the formation of an intramolecular hydrogen bonding. (Fig. 1)

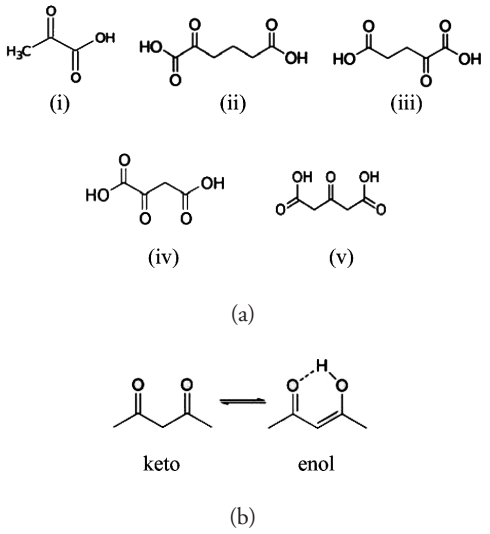

Figure 1. (a) Structure of the five keto acids selected for the study: (i) pyruvic acid, (ii) 2-oxoadipic acid, (iii) alpha-ketoglutaric acid, (iv) oxalacetic acid, (v) beta-ketoglutaric acid; and (b) Structure of keto-enol tautomers of oxalacetic acid and beta-ketoglutaric acid that gives more stability to their enol tautomers.

The radiolysis experiments show that keto tautomers are in general more easily decomposed than the enol tautomers, (Fig. 2). It is also evident by these experiments that keto acids are in general quite resistant to ionizing radiation, and with the exception of the oxalacetic acid, they can stand high doses of gamma ray (less than 50% destruction of the keto acids was observed after a dose of 53 kGy). In particular, pyruvic acid is extremely resistant to radiation, as also observed in previous studies [8, 9]. Oxalacetic acid is rapidly decomposed by ionizing radiation. It is also regenerated in a minimal extent during the irradiation process, probably by the same mechanism reported previously for the pyruvic acid [2,8,9]: a H radical adds to the carbonyl group yielding a radical (reaction 1) that by disproportionation forms the corresponding alcohol, malic acid (identified by using chromatography standards) and regenerated oxalacetic acid (reaction 2). Malic acid seems to be very reactive and decomposes rapidly in this system; so it is only detectable in small amount around 20 kGy.

$$HOOC(C=O)CH_2COOH + \cdot H \longrightarrow HOOC(\cdot C\text{–}OH)CH_2COOH \quad (1)$$

$$2HOOC(\cdot C\text{–}OH)CH_2COOH \longrightarrow HOOC(C\text{–}OH)CH_2COOH + HOOC(C=O)CH_2COOH \quad (2)$$

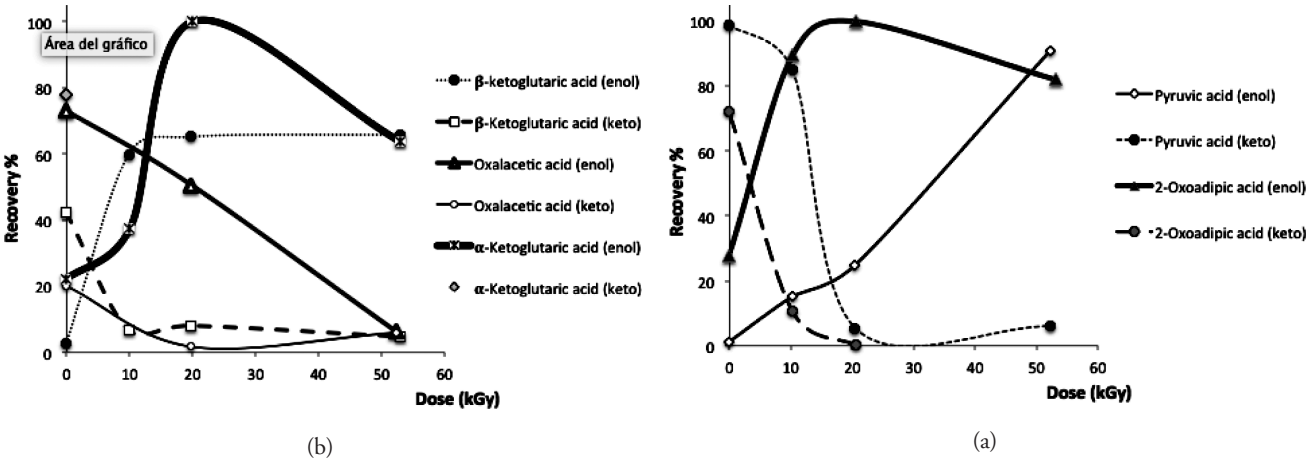

Figure 2. Effect of irradiation dose in the survival of aqueous solutions of keto acids: (a) pyruvic acid and 2-oxoadipic acid; (b) alpha-ketoglutaric acid, beta-ketoglutaric acid, and oxalacetic acid

That mechanism described before for the oxalacetic acid that might explain the presence of malic acid in the radiolytic products should operate for the alpha-ketoglutaric acid, producing hydroxyglutaric acid. However, by HPLC/UV technique it wasn't detected, so probably it is quite labile and it's easily decomposed by ionizing radiation and/or wasn't produced in a measurable extent by this analytical technique. Other products obtained by radiolysis of keto acids were spotted in small amounts among the irradiated samples, but there is need of more and different kind of analysis (like mass spectroscopy and gas chromatography) to fully identify them. For example, a little of lactic acid was observed after irradiating pyruvic acid with a dose of 53 kGy, as reported in previous researches [9]. Among the possible products to be identified in the samples can be the dimerization products (union of two radicals like the one described in reaction 1), and degradation products, like succinic, glyceric and glutaric acid.

4. Remarks

These preliminary results show the ionizing radiation's general effect on keto acids, demonstrating that at their natural pH values, the are stable in aqueous solution and can stand doses up to 53 kGy without completely decomposing. Keto-enol tautomerism tends to favor the enol tautomer after irradiation. This kind of research gives clues to a better comprehension of the chemical evolution that originated life on our planet. Evaluating stability of certain organic molecules, like keto acids, which are not easily obtained by radiolysis of hydrogen cyanide and other carboxylic acids in prebiotic conditions, is important to understand how these kinds of molecules may have become part of important metabolic cycles. More experimentation with keto acids considering different environmental conditions (different pH, dose, temperature) and additional analytical techniques may lead to more conclusions related to their probable prebiotic chemistry.

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