

Research Article

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Stability of α -ketoglutaric acid simulating an impact-generated hydrothermal system: implications for prebiotic chemistry studies

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Abstract

Life originated on Earth possibly as a physicochemical process; thus, geological environments and their hypothetical characteristics on early Earth are essential for chemical evolution studies. Also, it is necessary to consider the energy sources that were available in the past and the components that could have contributed to promote chemical reactions. It has been proposed that the components could have been mineral surfaces. The aim of this work is to determine the possible role of mineral surfaces on chemical evolution, and to study of the stability of relevant molecules for metabolism, such as α -ketoglutaric acid (α -keto acid, Krebs cycle participant), using ionizing radiation and thermal energy as energy sources and mineral surfaces to promote chemical reactions. Preliminary results show α -ketoglutaric acid can be relatively stable at the simulated conditions of an impact-generated hydrothermal system; thus, those systems might have been plausible environments for chemical evolution on Earth.

Introduction

Life originated on Earth possibly as a physicochemical process; thus, geological environments and their hypothetical characteristics on early Earth are essential for chemical evolution studies (Hazen, 2005). Chemical evolution, as Calvin defined, is the hypothetical period that starts when the Earth was formed and lasts until the first living beings appeared. In this time span, chemical reactions might have occurred, starting from simple compounds and transforming into more complex ones, forming living entities (Calvin, 1955). Those reactions could happen in one or more geologic scenarios, and for prebiotic chemistry studies, hydrothermal systems have been considered plausible sites for the origin of life (Colín-García *et al.*, 2016). A hydrothermal system forms when magma emerges on the surface and causes the heating of surrounding water (Nisbet and Sleep, 2001). A hydrothermal environment consists of two basic components: a heat source and a fluid phase. Heat fluids circulate at different temperatures and pressures, and the system could survive long enough to form anomalous concentrations of metallic minerals (Pirajno, 2009). Also, they constitute geochemical habitats that harbour microbial communities (Martin *et al.*, 2008). There are several types of hydrothermal systems. For chemical evolution studies, they can be classified in a simplified way on submarine, subaerial and impact-generated systems. Many of the prebiotic chemistry studies that involve hydrothermal systems focus on submarine environments, due to their association with magmas near to mid-ocean ridges, and with the origin of life on Earth (Colín-García *et al.*, 2016). This is due to the possibility that volcanism was more active on early Earth than it is today, and 'black smoker' vents could exist in abundance. However, subaerial systems could also exist if plate tectonics were already active. Acasta is a metamorphic heterogeneous complex, comprises rocks as tonalites, granitoides, granites, until ultramafic rocks. This place is an evidence that continental crust formed since 4.2 Ga (Iizuka *et al.*, 2006). Furthermore, they are a source of organic compounds, and those environments can harbour life without direct photosynthesis (Nisbet and Sleep, 2001; Martin *et al.*, 2008). In most solar system bodies that have a solid surface, impact cratering is the most important process of surface modification (Koeberl, 2013). Although it is still in debate, it has been proposed that during the Hadean, a heavy bombardment of asteroids and comets occurred on Earth, which means an increment of the impact rate at 4.0–3.8 Gyr (Kring, 2002; Gomes, *et al.*, 2005); hence, hydrothermal systems might have generated on primitive Earth as a result of those impacts. The record of lunar craters shows that the impact rate of size and flux decreased drastically after this period. Moreover, its end seems to coincide with the origin of life (Farmer, 2000). Even though impact events can produce environmental disturbances, the associated craters could have certain characteristics that make them adequate geological sites for chemical evolution, specifically those that develop the hydrothermal activity. The role of impacts on the origin of life has not been studied in detail (Cockell, 2006). In oceanic environments, the

Table 1. Changes on pH of the systems

System	pH _i	pH _f
Zeolite-AKG	3.5	6.5
Pyrite-AKG	3.5	6.5
Montmorillonite-AKG	5.8	3.5
Montmorillonite-AKG	5.8	6.5

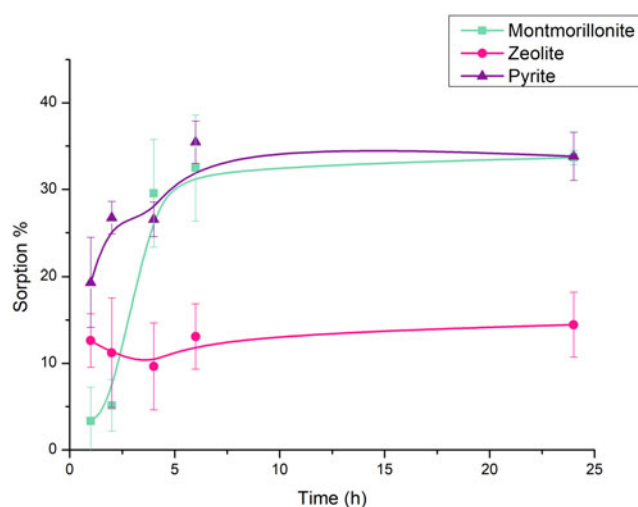
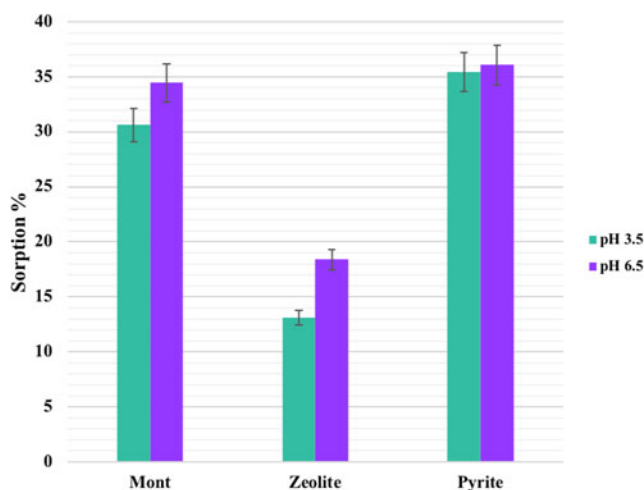
Table 2. Stability of AKG at different pH values

Time	Decomposition (%)			
	Initial	Week 1	Week 2	Week 3
Standard pH 3	0	2.2	1.2	1.8
pH 6	2.7	1.8	1.3	1.6
pH 8	2.7	2.0	2.7	2.5

problem that comes up is about the concentration of reactants because the volume of water is great. Thus, a plausible alternative to this problem can be impact-generated hydrothermal systems (Chatterjee, 2016). Those systems can work as a favourable geologic area for chemical evolution for three reasons: They have an energy source (thermal) for carrying out chemical reactions; a localized concentration of molecules can exist, and catalysis could arise; and they are systems that can persist for long periods (from 10 000 years to 2 Myr) (Daubar and Kring, 2001; Cockell, 2006). Mineral and clay mineral surfaces have been considered as possible as participants in the origin of life, thanks to their physicochemical properties, as they are capable of acting as catalysts, concentrating agents and as assembling molds for prebiotic molecules (Bernal, 1951; Goldschmidt, 1952; Cairns-Smith, 1966; Hazen, 2012). For this reason, in prebiotic chemistry studies, it is important to take them into account and find the role they represent in this research area (Negrón-Mendoza, 2004; Hazen, 2005; Hazen and Sverjensky, 2010; Cleaves *et al.*, 2012).

Along with thermal energy, ionizing radiation could play an important role in chemical evolution because, on the early Earth, the levels of radiation were significantly higher than they are today. Radiation dose from geologic emitters has changed because of the evolution of the continental crust and the relative abundances of radionuclides (Karam and Leslie, 1999). Also, the intensity of ionizing radiation coming from the exterior of the planet was higher. Chemical changes produced by this type of energy could be the cause of modification of prebiotic molecules that led to the subsequent emergence of life, absorbing energy either directly or indirectly through the presence of other radiolytic products on the medium (Zagórski and Kornacka, 2012). Production of radiolytic molecules relevant for life has been considered in primordial aqueous environments due to ⁴⁰K decay (Draganić, 2005).

α -keto acids are compounds that have a carbonyl group adjacent to a carboxylic group. Keto acids are formed as intermediates during metabolic interconversions of sugars, carboxylic acids and amino acids. Those analogous to natural amino acids have great importance in intermediary metabolism. Other metabolic processes in which α -keto acids play an important role are the Krebs cycle and glycolysis. As the precursor to citric acid,

**Fig. 1.** AKG sorption onto different minerals.**Fig. 2.** Differences in sorption capacity of minerals when pH is modified.

Acetyl-CoA is exposed to chemical conversions in which keto acids such as α -ketoglutaric and oxaloacetic acid are involved (Nelson and Cox, 2012). α -ketoglutaric acid (AKG) is a small molecule ($C_5H_6O_5$) that possibly played a role in the period of chemical evolution; for this reason, the aim of this work is to study the behaviour of this molecule under radiation and thermic energy conditions, simulating chemical reactions that might have occurred in a primitive environment such as impact-generated hydrothermal system.

Materials and methods

Analytical techniques

For the analysis of the α -ketoglutaric acid, a derivatization method is needed. In this work, o-phenylenediamine (OPDA) was used as a derivatizing agent, according to Montenegro *et al.* (2011). The chromatographic analysis was carried out on a UHPLC UltiMate 3000 chromatographic system (Thermo Scientific®, USA), with a UV-Vis Dionex UltiMate 3000 VWD

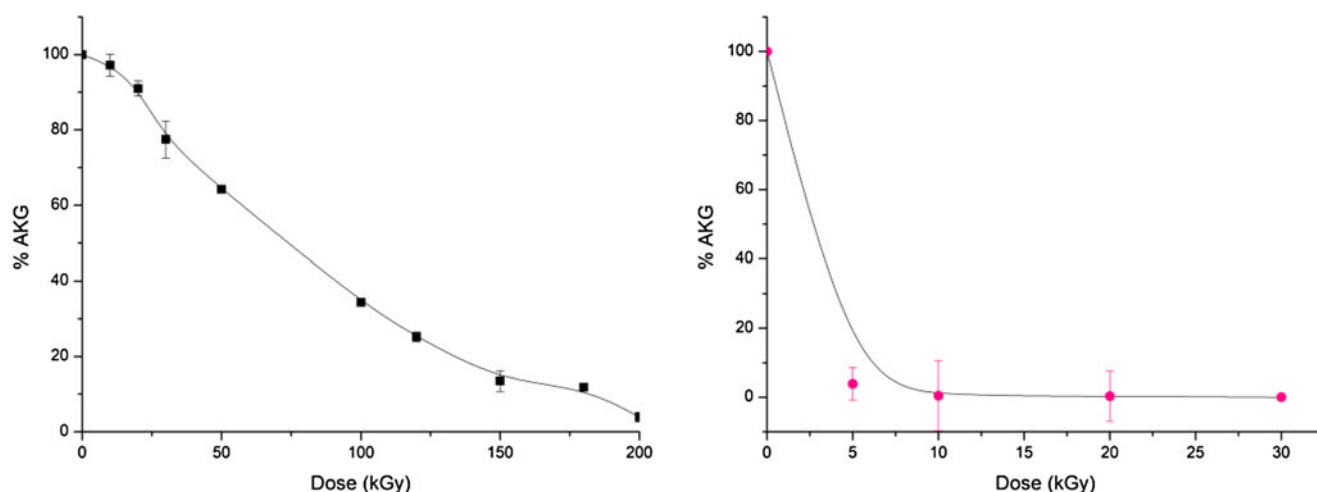


Fig. 3. Decomposition of AKG by γ radiation (Left: irradiation of 0.1 M solution. Right: irradiation of 1×10^{-3} M solution).

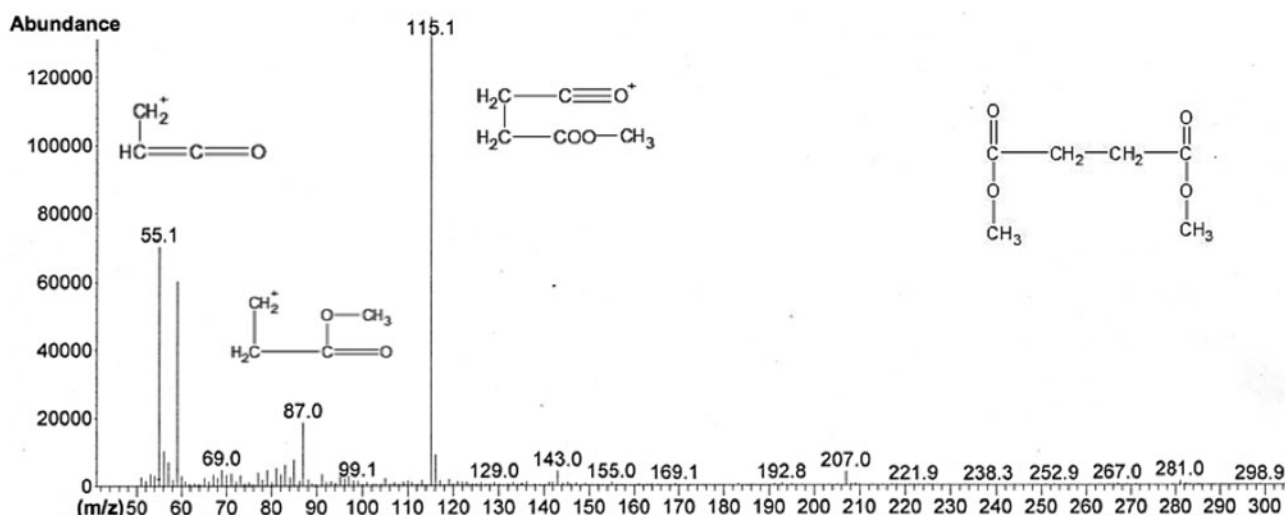


Fig. 4. Mass spectrum of succinic acid (methyl ester) formed by irradiation of AKG at 30 kGy.

(Thermo Scientific®) detector and a Halo® C8 column ($50 \times 4.6 \mu\text{m}$) for the separations. The mobile phase was prepared with 90% ammonium acetate (8 mM, pH 4.5) and 10% methanol at 0.3 ml min^{-1} at 25°C . A fixed sample volume injection of 20 μl was used. The samples were detected at 340 nm. In addition, gas chromatography was used for the analysis of AKG and radiolytic products. The instrument was a gas chromatograph HP-5890A with a capillary column filled with methyl silicon. The samples were derivatized to their corresponding methyl ester, according to Negrón-Mendoza and Ponnampetuma (1976).

Materials and glassware

Three different minerals were used for the experiments: SWy-2 Na-montmorillonite (Source of Clay Minerals Repository, Wyoming, USA), pyrite (from Spain) and zeolite (stilbite and heulandite, from Pune, India). AKG was from Sigma Aldrich®. To avoid organic contamination on irradiation experiments, glass material was treated according to radiation chemistry procedures (Draganić, 2005).

pH stability analysis

To learn about the behaviour of AKG in basic pH, stability experiments were carried out. The pH of AKG standard solution was 3, and generally, in impact-generated hydrothermal systems, the reported pH range was slightly alkaline or near neutral (Osinski, 2005; Osinski, *et al.*, 2005). Three samples were analysed: The first one was the standard solution without any pH modification. For the second, a pH modification to 6.5 was done using NaOH 0.01 M. For the last sample, the pH was increased to 8. The stability was evaluated immediately after the pH modification, as well as 1, 2 and 3 weeks later.

Sorption studies

Before the assays, mineral samples were treated to remove organic contamination, using a 3% KOH solution (10 ml g^{-1} mineral), stirring for 30 min, rinsing with distilled water, stirring again for 30 min with a 3% HNO₃ solution (10 ml g^{-1} mineral), rinsing and letting dry.

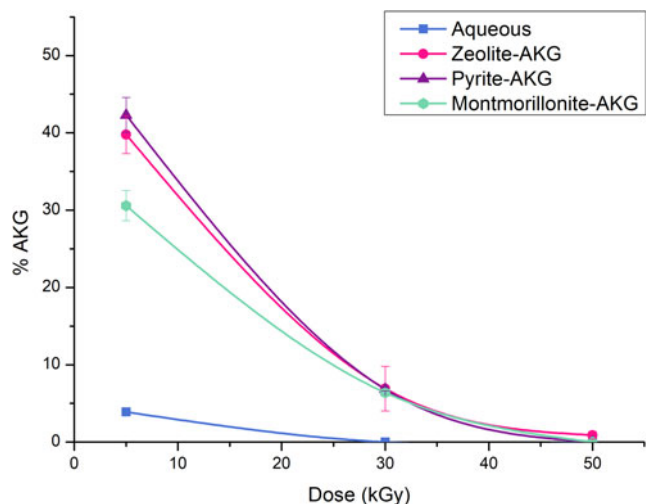


Fig. 5. Comparison of the radiolysis of aqueous AKG and mineral-AKG systems.

Sorption assays were performed using 2.5 ml of aqueous standard solution of α -ketoglutaric acid 0.001 M and 50 mg of mineral (mineral-AKG systems). Samples were stirred at different times (1, 2, 4, 6 and 24 h) in centrifuge polyallomer tubes 16×76 mm (Beckman Coulter®). Then, the tubes were centrifuged at 26 000 rpm (Beckman Coulter Allegra 64R® centrifuge) for 25 min for the separation of phases. The volume needed for the derivatization was taken from the liquid phase. The sorption percentage was calculated considering the change in the peak area in relation to the standard peak. Sorption studies were done in triplicate.

Sorption studies at different pH

When zeolite or pyrite interacts with the aqueous solution of AKG, the pH of the system is 3.5 (pH_i). On the other hand, the montmorillonite-AKG system pH is 5.8. A sorption test with fixed pH (pH_f) was conducted to observe if there is a difference in sorption capacity in these systems at 24 h fixed time (Table 1).

Radiolysis

Aqueous solution

Aside from the thermal energy effect, ionizing radiation was selected as another energy source on early Earth. Samples of tri-distilled aqueous solutions of AKG 1×10^{-3} M were irradiated with γ rays from a ^{60}Co source located at the Gammabeam 651-PT of the Instituto de Ciencias Nucleares, UNAM. Radiation doses were from 5 to 50 kGy, and the dose intensity was 167 Gy min^{-1} . Radiolysis experiments were done in duplicate and with oxygen-free solutions. Additionally, GC-MS analysis was performed for the identification of radiolytic products (carboxylic acids) through their methyl esters.

Mineral-AKG systems

To study the effect of the presence of minerals when AKG is exposed to γ radiation, samples of each mineral and AKG were prepared as in section 'Materials and glassware' at a fixed time of contact of 24 h. Once the contact time was reached, samples

were irradiated at 5, 30 and 50 kGy, then centrifuged, and the supernatant was collected.

Thermolysis

Thermolysis assays were carried out with oxygen-free 1×10^{-3} M aqueous solution of AKG. Two different systems were used for this purpose. The first one consisted of a heating static system composed of a flask assembled to a condensation column for the recirculation of organic solvents. The organic solvent was contained inside the flask while it was heated to its boiling point at 582 mm Hg. The flask had four orifices to insert tube samples; these tubes did not come in direct contact with the solvent. Three different solvents were used to reach different temperatures: toluene, dimethylformamide and nitrobenzene (100, 135 and 180°C , respectively). The second system was a temperature-controlled ($\pm 2^\circ\text{C}$) stove (Venticell 22 Eco line MMM Group®). Sealed glass ampules were used as sample containers for this system. The temperature used in the stove was 180°C .

Results

pH stability analysis

The measurements concerning the stability of AKG 10^{-3} M at different pH ranges indicate that the molecule is stable after 3 weeks of the preparation of the standard solution (pH 3) and the fixed pH solutions (Table 2).

Sorption assays

All three minerals showed sorption of AKG; pyrite and montmorillonite have more sorption capacity (35%) than zeolite (15%). Poor sorption was observed at 1 h of contact. However, the sorption increases at 6 h and the maximum is reached at 24 h, where sorption capacity seems to remain constant (Fig. 1).

Sorption at different pH

Figure 2 shows that sorption capacity slightly increases when pH is higher (pH_f from Table 1), especially with zeolite ($\sim 5\%$), these results suggest that if the environment has pH gradients between 3.5 and 6.5, sorption capacity has no major alterations.

Radiolysis

Aqueous solutions

Decomposition of AKG was followed at different radiation doses. AKG shows to be labile when it is exposed to γ radiation (Fig. 3). A 0.1 M solution was made for a better tracking of decomposition, but the effect of radiation in both irradiated concentrations (0.1 and 1×10^{-3} M) was the same.

GC-MS analysis showed that the main radiolytic product is succinic acid (Fig. 4). Malonic and glutaric acids were also detected.

Mineral-AKG systems

The results of the irradiation of mineral-AKG systems demonstrate that all minerals have a protective effect versus radiation, preventing AKG decomposition at 5 and 30 kGy doses. It was observed (Fig. 5) that pyrite has a high protective effect, followed

Table 3. Thermolysis of AKG 1×10^{-3} M at different conditions

System	Temperature (°C)	Time (h)	Decomposition (%)
Static-toluene	100	6	–
		24	–
		44	–
		92	–
Static-dimethylformamide	135	6	–
Static-nitrobenzene	180	3	–
Stove	180	6	27
	180	8	27

Table 4. Impact-generated hydrothermal system and their main characteristics

Crater	Location	Diameter	Minerals	Age of formation	Physicochemical Characteristics	References
Houghton	Devon Island, Canada	23 km	Calcite, marcasite, selenite, fluorite, pyrite, goethite	39 My	<i>T</i> early stage ~500°C, main stage ~200–100°C. pH: variable, slightly alkaline to neutral. Acidic on main stage (suggested by marcasite deposit) Estimated lifetime: 10 000 years	Osinski <i>et al.</i> (2005)
Ries	Bavaria, Germany	~24 km	Montmorillonite, illite, saponite, zeolites, calcite, albite, chlorite, K-feldspar, hematite, goethite	14.3–14.5 My	<i>T</i> main stage ~200–100°C. pH slightly alkaline	Osinski (2005).
Popigai	Siberia, Russia	100 km	Calcite, zeolites, pyrite, quartz, chlorite, saponite, smectites	36 Ma	Zeolite, calcite and pyrite indicate hydrothermal alteration at low temperatures. Neutral to slightly alkaline pH with variable zones (lower pH)	Naumov (2002).
Sudbury	Ontario, Canada	~250 km	Chlorite, actinolite, sulphides, sulphates, smectites, Zn-Pb-Cu deposits	1.85 Ga	Hydrothermal system with <i>T</i> < 260°C. Temperature gradients 100°C km ⁻¹	Ames <i>et al.</i> (2006).

by zeolite and montmorillonite, respectively. At doses of 50 kGy, the systems exhibit total decomposition of AKG.

Thermolysis

Several experiments were conducted at different times and temperatures for thermolysis of AKG. Table 3 shows the obtained results. Some problems were encountered in managing samples in the static system at temperatures above 100°C; thus, a temperature-controlled stove was used. AKG seems to be stable in high-temperature conditions. Further analysis is needed to track the stability of the compound.

Discussion

Considering AKG as a possible precursor for the production of different molecules relevant for chemical evolution and through the study of the stability of this compound, we can suggest clues about its possible availability on early Earth. AKG is stable in alkaline and high-temperature conditions, notwithstanding it is labile under high radiation doses. Minerals such as montmorillonite, pyrite and zeolite can act as concentrators and protectors

of α -ketoglutaric acid. Minerals and physicochemical variables for this study were selected based on a review of the literature, shown in Table 4. Preliminary results show that one of the main radiolytic products in aqueous solution is succinic acid, which suggests a dehydroxylation and decarboxylation reactions. Analysis of the radiolytic products of all three mineral-AKG systems is needed to understand the nature of the reactions. It has been reported that in the radiolysis of AKG sorpted onto montmorillonite, the number of radiolytic products decreases, and the main decomposition pathway is decarboxylation, producing succinic acid and CO₂ (Negrón-Mendoza and Ramos-Bernal, 1998).

The purpose of choosing AKG is because in previous studies (Negrón-Mendoza and Ponnampereuma, 1976; Cruz-Castañeda *et al.*, 2014; Negrón-Mendoza and Ramos-Bernal, 2015; Negrón-Mendoza *et al.*, 2018), starting from the irradiation of a member molecule of Krebs cycle (i.e. acetic, citric, succinic acids), various compounds (also Krebs cycle members) are produced, although AKG is not found. To get an insight for the lack of its detection, we compare the results of this work with the radiolysis of some carboxylic acids, and from these data, we calculate according to Criquet and Karpel Vel Leitner (2011,

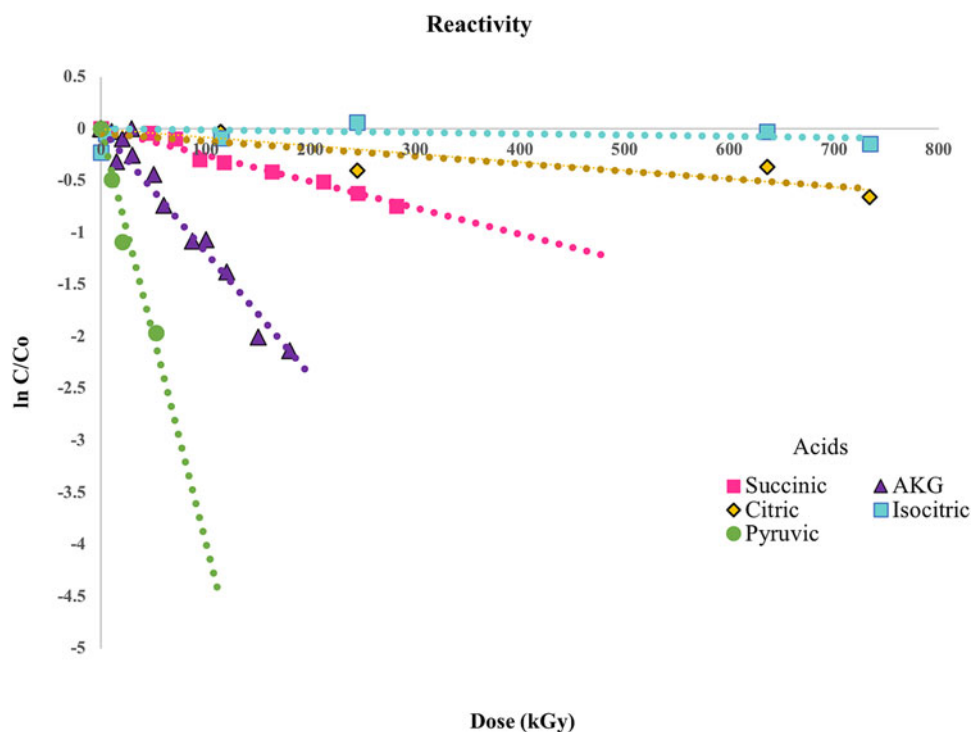


Fig. 6. Decomposition of some Krebs cycle carboxylic acids in aqueous solution, acidic pH, exposed to different doses of γ radiation.

Table 5. Dose constants of some carboxylic acids

Acids	k	Reference
Isocitric	3×10^{-5}	Negrón-Mendoza and Ramos-Bernal (2015)
Citric	8×10^{-4}	Negrón-Mendoza and Ramos-Bernal (2015)
Succinic	3.5×10^{-3}	Cruz-Castañeda <i>et al.</i> (2014)
AKG	1.19×10^{-2}	This work
Pyruvic	3.99×10^{-2}	(unpublished work)

2012), parameters of degradation versus radiation dose. These results are presented in Fig. 6, where C_0 is the initial concentration of the acid, C is the concentration at dose D in kGy, and k is the dose constant (linearly, the slope is k). It is important to remark that this equation is only descriptive and is not a model of the physicochemical processes of the radiolysis, but it gives a simple approximation about the reactivity towards the degradation of the compounds. These calculations show that citric and isocitric acids are the most stable acids under high radiation doses, while pyruvic and α -ketoglutaric acids (both keto acids) are the most reactive and the decomposition occurs at lower radiation doses with a high k (1.19×10^{-2}) compared, for example, with isocitric acid (3×10^{-5}). This lability under high radiation conditions may explain why it is not easy to detect AKG in prebiotic experiments. Nevertheless, AKG is converted into products with higher stability (i.e. succinic acid), as seen in Fig. 4. Table 5 shows the k values obtained.

Conclusions

Studies about impact-induced hydrothermal systems and their role in prebiotic chemistry are scarce. AKG is capable of existing

on environments such as impact-induced hydrothermal systems, which are complex geological systems that present different characteristics, such as pH and temperature gradients, and might also have existed on primitive Earth. AKG is easily degraded under a high radiation field, despite this fact, minerals present in those environments could support the persistence of AKG by concentrating molecules for further reactions and protecting them through inherent and external factors like heat and ionizing radiation, respectively. Other metabolism-relevant carboxylic acids can be produced by AKG decomposition, such as succinic acid.

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