



Stability of Pyruvic Acid Adsorbed Onto Clays and Exposed to Ionizing Radiation: Relevance in Chemical Evolution

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ARTICLE INFORMATION

Received: October 10, 2019

Accepted: January 27, 2020

Published online: February 28, 2020

Keywords:

Chemical evolution, Pyruvic acid, Clays, Gamma radiation

ABSTRACT

Chemical evolution studies focus on the synthesis and stability of organic molecules during various transformative physicochemical processes. Gaining insight into the possible mechanisms behind these processes requires the use of various energy sources and catalysts that can produce such transformations. In this work, ionizing radiation (⁶⁰Co) was used as a source of energy, and two clays with different exchangeable cations-sodium and iron (III)-were combined with pyruvic acid, a key alpha keto acid in metabolism. The samples of pyruvic acid were prepared at a concentration of 0.01 M; then, adsorption experiments were carried out by combining sodium or iron montmorillonite at different times. The amount that adsorbed onto iron montmorillonite was greater than the amount that adsorbed onto sodium montmorillonite. Samples of alpha keto acid at the same concentration were irradiated-in the absence of clay-at 0 to 146.1 kGy and at two pHs (6.7 and 2.0). The suspended samples with sodium and iron clay were then irradiated at the same doses. The results show that keto acid decomposes more quickly at more acidic pHs. The main reaction to irradiation without clay involves the dimerization of pyruvic acid, and 2,3-dimethyltartaric acid is the majority product. When irradiated in the presence of clay, the main reaction is decarboxylation, and acetic acid is the majority product. The exchangeable cation type modifies the interactions between the organic molecule and the solid phase. The percentage of recovered pyruvic acid is higher for iron montmorillonite than for sodium montmorillonite.

DOI: [10.15415/jnp.2020.72011](https://doi.org/10.15415/jnp.2020.72011)



1. Introduction

The use of energy from external sources to boost chemical reactions is inherent to life [1]; a classic example is photosynthesis. As a result, researchers who are studying chemical evolution and prebiotic chemistry seek to find the combinations of chemical and physical factors in which a source of abundant energy and an environment produce the necessary conditions for the emergence and evolution of life [2]. The external energy available on the Precambrian Earth came from geothermal sources (e.g., hydrothermal vents), impact shock waves, ultraviolet solar radiation, and electric discharges [1], and even ionizing radiation from radionuclides.

Pyruvic acid is an important molecule in the prebiotic context due to the central role that it plays in many known metabolic pathways. Pyruvic acid also serves as an intermediary molecule in both aerobic and anaerobic organisms [1]. Abiotic synthesis of pyruvic acid is possible at the high pressures and organometallic phases seen in hydrothermal and volcanic environments [3]. Pyruvic acid has also been

produced using the formamide (NH₂CHO) condensation reaction, as catalyzed with various meteorite samples [4]. In addition, it has been detected (in the parts-per-billion range) in extraterrestrial bodies such as carbonaceous chondrites [5], which indicates a possible prebiotic and/or interstellar origin. Various reactions with pyruvic acid as the main reagent have been studied. Experiments performed under complex hydrothermal conditions have produced molecules with high molecular weights. Some of those molecules are amphiphilic, which means that they easily self-assemble into vesicular or aqueous photoactive structures [6].

This study, explains why pyruvic acid is relevant for prebiotic chemistry. In other studies, interactions with minerals have been shown to increase the stability of organic compounds [7]. The clays that were present in the primitive Earth may have provided protection against gamma radiation; this possibility is part of this study. Sodium montmorillonite was chosen as the starting mineral phase, as it existed around 3.8 Ga [8], when chemical evolution is situated. This study also considers the effect of the

exchangeable cation inside the interlaminal canal. Iron (III) was used for this because it is among the most abundant elements in hydrothermal and volcanic environments.

2. Methodology

2.1 Preparation Clays

The sodium clay used in the reactions (Na^+ -montmorillonite SWy-1) was obtained from the Clay Minerals Repository of the Clay Minerals Society at the University of Missouri. The iron clay (Fe^{3+} -montmorillonite) was prepared from the sodium clay via an ion-exchange reaction [9] in which prepared 1 N solutions of $\text{FeCl}_3 \cdot 5\text{H}_2\text{O}$ were used to exchange the Na^+ cations with the desired Fe^{3+} ions.

2.2 Adsorption of Pyruvic Acid in Clays

Aqueous solutions of pyruvic acid were prepared at their natural pH (6.67) and at a concentration of 0.01 M. All samples were met the Sigma-Aldrich standard for high purity (99%). Aliquots of 3 mL were added to 100 ± 0.01 mg of sodium or iron clay, and the pH was modified to one of three values (2.01, 6.67, or 8.5) with HCl or NaOH (both 0.01 M). The samples were then stirred in a Thermo Scientific (Model 4632) multi-tube rotator for various lengths of time. They were then centrifuged (Allegra 64R) at 23,000 rpm for 30 minutes. The supernatants were read in a high-performance liquid chromatograph (HPLC), Perkin Elmer Series 200, with an ultraviolet detector. The chromatographic conditions included a 300×7.8 mm anionic exclusion column (Alltech); a mobile phase of 90% H_2SO_4 (0.0015 M) and 10% water; a 0.6 mL/min flow rate; and a 20 μL sample size.

2.3 Samples Irradiation

Solutions of pyruvic acid without clay.

The glassware was treated according to the procedure recommended by Draganic and Draganic [10]. Aqueous solutions of pyruvic acid were prepared at their natural pH value (6.7) and at pH 2; the pH was modified using 0.01 M HCl. All samples were prepared with triple distilled water according to standard radiation-chemistry techniques [10].

Fresh solutions of alpha keto acid were prepared in the absence of oxygen (which was removed by saturating the solutions with argon) and then irradiated by exposing them to various doses of gamma radiation from a cobalt-60 gamma-ray source (Gamma beam 651 PT). The dose interval was from 0 to 146 kGy. After the irradiation, the samples were analyzed using a high-performance liquid chromatograph with ultraviolet detection. To identify the radiolysis products, standard solutions of the following acids were injected: citric, oxalic, tartaric, glyceric, maleic, malic, malonic, glutaric, lactic, succinic, acetic, and propionic.

Solutions of pyruvic acid with clays.

To create suspensions, 100 ± 0.01 mg of each clay was mixed with 3 mL of pyruvic acid solution (0.01 M). The samples were then mixed in a vortex and agitated for various lengths of time in order to obtain the maximum sorption. After the samples were treated (in the same manner as the samples without clay), they were irradiated (at the same doses as the other samples). The recovery of pyruvic acid from the supernatant (remnant) was then measured. To recover the pyruvic acid that had adsorbed onto the clay, the supernatant was treated with a solution of NaOH at pH 8, and the concentration of pyruvic acid was then normalized to the maximum amount extracted.

3. Results and discussion

3.1 Adsorption of Pyruvic Acid in Clays

Figure 1 shows the adsorption of pyruvic acid with two clays at pH 2. The sorption of pyruvic acid was greater in the iron montmorillonite than in the sodium montmorillonite, however after 30 minutes of contact with iron montmorillonite, the pyruvic acid had reacted, forming an unidentified reaction product. Which indicates the ability of iron present in montmorillonite to produce other reactions in pyruvic acid.

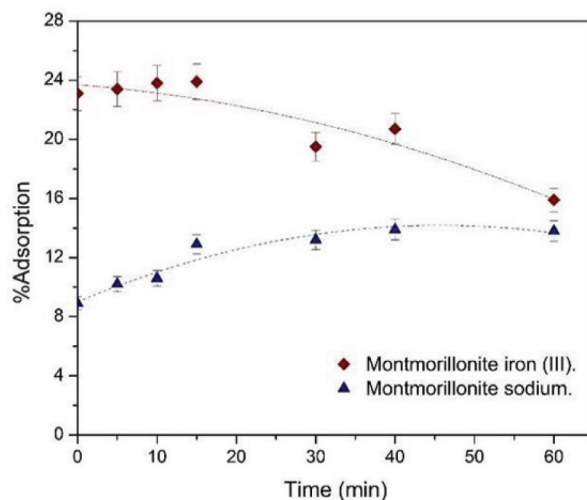


Figure 1: Adsorption of pyruvic acid in sodium and iron montmorillonite at pH 2.

3.2 The Effect of pH in the Radiolysis of Pyruvic Acid

Figure 2 shows the effect that changes in the solutions' pHs have on the relationship between decomposition and irradiation. Because the decomposition rate is higher for more acidic pHs, the main decomposition occurs through

the attack of the radicals H and OH (from the water's radiolytic products).

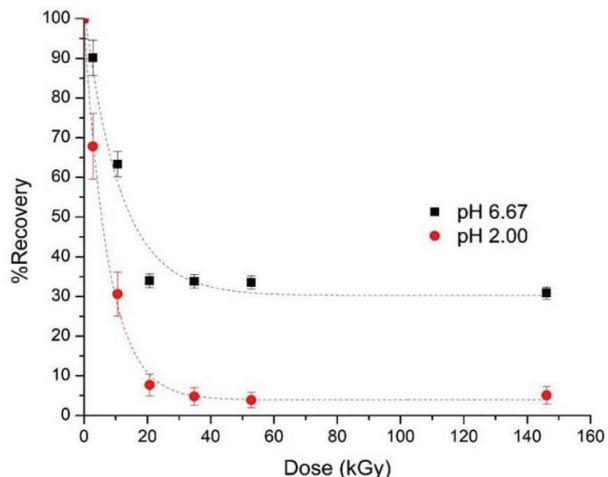


Figure 2: Decomposition of pyruvic acid as a function of pH and irradiation dose.

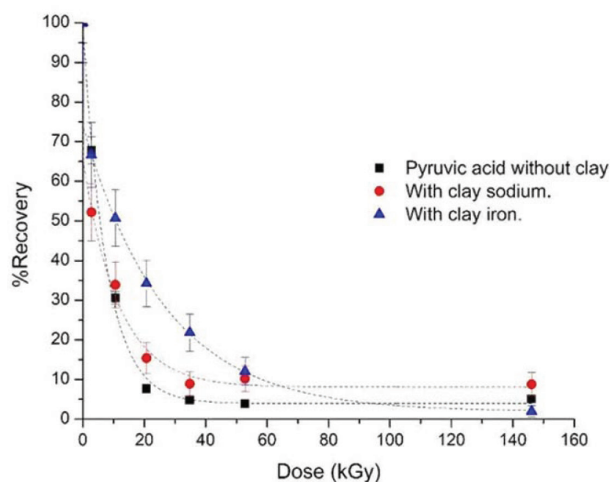
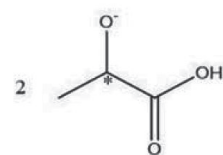
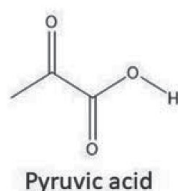
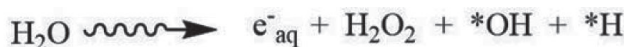


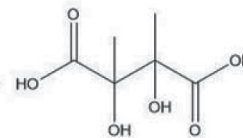
Figure 3: Decomposition of pyruvic acid (pH 2) in a clay suspension as a function of the irradiation dose.

The water's radiolytic products initiate the mechanism of decomposition for pyruvic acid in aqueous solutions. Figure 4 shows one possible mechanism.

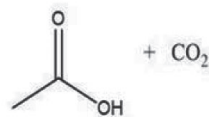
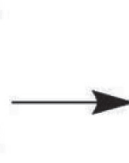
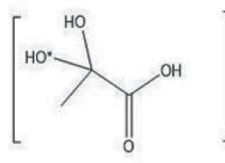
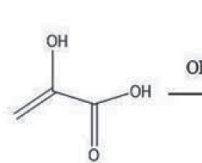
Radiolysis of water:



Dimerization (reaction of two identical fragments).



2,3-dimethyl tartaric acid.



Acetic acid.

Decarboxylation (loss of CO₂)

Figure 4: Proposed mechanism for the radiolysis of pyruvic acid.

The dependence of the formation of the products is observed with the absence or presence of the clays. The two main products are 2,3-dimethyl tartaric acid and acetic acid.

Conclusions

The pyruvic acid molecule decomposes more quickly at acidic pHs than at basic pHs. The presence of clay modifies the decomposition of pyruvic acid. A clay's exchangeable

cation modifies an acid's reactivity; for instance, iron (III) catalyzes the formation of an unidentified product.

The formation of acetic acid and 2,3-dimethyl tartaric acid are important in chemical evolution, since under the conditions of this simulation experiment, products with greater and lesser amount of carbon bonds are obtained. Further studies will be needed, such as identifying more decomposition products.

Acknowledgements

This work was supported by DGAPA IN210119. We thank the technical support from Chem. Claudia Camargo, Phys. Francisco García Flores, M. Sc. Benjamín Leal Acevedo.

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Journal of Nuclear Physics, Material Sciences, Radiation and Applications

Chitkara University, Saraswati Kendra, SCO 160-161, Sector 9-C,
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Volume 7, Issue 2

February 2020

ISSN 2321-8649

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