

CARBOXYLIC ACID TRANSFORMATIONS IN THE PRESENCE OF MINERAL SURFACES. K. N. Johnson¹, I. R. Gould¹, L. B. Williams², H. E. Hartnett^{1,2} and E. L. Shock^{1,2}, ¹Arizona State University (School of Molecular Science, Tempe 85287-1404, Kristin.N.Johnson@asu.edu), ²Arizona State University (School of Earth and Space Exploration, Tempe 85287-1404).

Introduction: Carboxylic acid functional groups are present in biological molecules such as amino acids and lipids, and are abundant within carbonaceous chondrite meteoritic material. By understanding the transformations of carboxylic acids that are possible in the presence of specific minerals, we can begin to understand the types of processing available to early pre-biotic reactions on Earth as well as on other worlds. We have performed experiments under hydrothermal conditions (300°C and 1000 bar) to analyze the effects of minerals on carboxylic acids. Previous studies of carboxylic acid reactivity with minerals have focused on simple molecules such as acetic acid and valeric acid [1] and [2]; in these studies iron-bearing minerals increased the rate of decomposition for the molecules of study. The carboxylic acids used here (phenylacetic and benzoic) differ from those in earlier work by the addition of a phenyl ring, allowing us to use the molecule as a model compound in our investigations of mechanistic pathways for product formation, a method employed in the investigation of other functional groups by members of our laboratory [3, 4, 5]. Decarboxylation (i.e., $\text{RCO}_2\text{H} \rightarrow \text{RH} + \text{CO}_2$) is the major reaction pathway for carboxylic acids in the absence of minerals under hydrothermal conditions, but we have observed the formation of new carbon-carbon bonds in the presence of oxide minerals. By holding crystal structure constant, we can investigate the specific mineralogic properties that govern organic transformation reactions. Ensuing generalizations allow predictions to diverse geologic settings on Earth or other worlds.

In the absence of minerals, phenylacetic acid ($\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$) decarboxylates in hydrothermal experiments to yield toluene and CO_2 [6]; the mechanism of decarboxylation was studied extensively by Glein through the use of model benzene ring compounds and substituent groups.

In the present study, hydrothermal experiments in the presence of spinel (MgAl_2O_4) yield the results of decarboxylation as well as additional products. Though decarboxylation remained the dominant pathway, formation of a symmetrical ketone structure (dibenzylketone) indicated the activation of additional product pathways in the presence of a mineral surface. Once formed, the ketone became a reactant for an

additional step of radical decoupling, analogous to that described previously [4].

In hydrothermal experiments of phenylacetic acid in the presence of magnetite (Fe_3O_4), additional product pathways were observed. The presence of magnetite did not enhance the rate of toluene production from decarboxylation, but did activate the formation of ketones, diphenyl alkanes and alkenes. In contrast with the experiments using spinel, benzoic acid was formed and behaved as a reactant in a new series of reactions including decarboxylation, as well as formation of an asymmetrical ketone with the phenylacetic acid starting material.

Not all minerals are capable of producing even the ketone organic reaction. Experiments with quartz (SiO_2) did not differ from the results in water alone. Hematite (Fe_2O_3) was capable of facilitating the same reactions observed for magnetite, including the formation of benzoic acid, but to a much lesser extent. By comparison, corundum (Al_2O_3), demonstrated the formation of ketone to a lesser extent than hematite, but did not result in the formation of benzoic acid.

Spinel and magnetite facilitate the formation of larger products from phenylacetic acid, with a corresponding increase in complexity. The extent and array of reactions appears to be a result of metal centers present in their respective formulas. Possible reasons for the differences observed between mineral experiments include the zero point of charge which influences the charge distribution on the mineral's surface, mineral structures, redox states, available surface area and electron mobility along band gaps of specific minerals.

The variety of minerals present on a world can drastically change the types of organic reactions available to pre-biotic reactions. To understand the kind of chemistry that could exist on a habitable world, we much know the extent of pre-biotic chemistry available to emergent life.

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