

High Pressure Hydrothermal Chemistry of Citric Acid and Related Acids

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Abstract High pressure hydrothermal reactions were run using sealed gold tube reactors and an internally heated high pressure apparatus. The reaction conditions varied from 150 to 350° C and from 0.5 to 5.0 Kb. The effects of pressure on a wide range of reactions was clearly evident and in some cases counter intuitive. Although high pressure clearly favored hydration reactions, decarboxylation reactions were greatly accelerated. In the system pyruvic acid - water, the chemistry was dominated by Aldol and Diels-Alder cycloaddition chemistry leading to a broad array of functionalized aromatic molecules which exhibited micellar qualities. The system citric acid - water yielded an interesting reaction network characterized by a number of isomeric equilibria. The effects of pressure operated on displacing the various equilibria towards specific isomers. The effects of pH on the citric acid chemistry also had significant control on metastable equilibria. These results are being integrated into a larger study of the feasibility of biochemistry emerging from the intrinsic organic chemistry associated with hydrothermal vents.

Experimental

All reactions were run in sealed (welded) gold tube reactors. Pressure and temperatures of interest were obtained using an internally heated high pressure apparatus. Following reaction, samples were quenched. Each sample was weighed before and after reaction to ensure sample integrity. Samples tubes were immersed in vials of BF₃/propanol, a known quantity of pentadecane was added as a standard, and heated at 90 °C for 1 hr. to esterify products. The derivitized products were extracted in dichloromethane, dried over NaSO₄, and analyzed with gas chromatography with mass spectrometric detection.

Results and Discussion

In order to better understand the potential for organic synthesis and the feasibility of biochemical reactions under extremes of pressure and temperature characteristic of deep sea hydrothermal vents we have begun to explore the high pressure aqueous chemistry of a number of potentially relevant biochemicals. In particular we have sought to address the question of whether metabolism recapitulate biogenesis, i.e. we are focusing on establishing whether the various metastable equilibria among the principal components of the tricarboxylic acid cycle favor anabolic synthesis at high pressures and temperatures. The results presented below involve high-pressure hydrothermal experiments probing the reactions and stability of pyruvic acid and citric acid, respectively, in CO₂ - H₂ bearing aqueous fluids in the temperature range of 150-350 °C and 0.5 to 5.0 Kbar. At this stage our principal focus is in identifying the effect of pressure on reaction selectivity in systems that exhibit multi-channel reactions. Towards this end, we have focused on two relatively simple systems in order to gain fundamental information on the kinetics of reactions that typify biological processes, albeit under strictly abiotic conditions. The data derived will provide a foundation for subsequent work on the potential for abiotic synthesis of classically bio-organic compounds at extremes of temperature and pressure, conditions that typify deep ocean hydrothermal vents.

In the pyruvic acid system we set out to determine whether pressure would favor the synthesis of oxaloacetic acid through an electrophilic addition of CO₂ at elevated temperatures. Thus far, have not revealed any evidence for the synthesis of oxaloacetic acid. Other interesting reactions, however, are operative within this pressure and

temperature regime. We observe substantial product yields from three reaction channels operating in series and parallel. One of these channels yields appreciable quantities of the five carbon diacid, methyl succinic acid, that forms through a cascade of reactions moving (evidently) through a number of intermediates. There is evidence that this reaction may be concerted (Figure 1). The reaction pathway is superficially similar to the citric acid cycle with the exception of the initial step; i.e. the initial step involves the formation of an Aldol condensation product rather than an electrophilic addition reaction.

A second reaction channel involves the straightforward de-carboxylation of pyruvic acid and is not particularly interesting beyond helping to establish the limits of pyruvic acid stability. On the other hand, the third reaction channel produces a very interesting and complex suite of compounds with amphiphilic qualities (Figure 2). This particular reaction channel operates, in general, through sequential Aldol condensations, Diels-Alder cyclo-additions, decarboxylations, dehydrations, dehydrogenations, and/or hydro-genations. Significant and systematic pressure and temperature induced changes in the distribution of molecules within this suite are observed.

In general, we observe that pyruvic acid is destabilized with increases in temperature and pressure, leading to the formation of the aforementioned products. Clearly evident are pressure effects manifested in the yields of methyl succinic acid and within the amphiphilic suite of compounds.

The system citric acid in CO_2 - H_2 bearing aqueous fluids is equally interesting. As would be expected, the principal reactions involve mono, double, and triple decarboxylations; with and without dehydration, as well as hydrogenation (Figure 3). The product distributions exhibit strong temperature and pressure selectivity (Figure 4). In general the citric system under the range of conditions explored exhibits catabolic chemistry. This is due, principally the apparent irreversibility of acid catalyzed decarboxylations. Surprisingly, pressure enhances the kinetics of these reactions, thus greatly accelerates the catabolic evolution of the system. The citric acid system, does however, serve as a useful and relatively simple system to explore the role of pressure in essentially pure ionic aqueous organic chemistry.

Acknowledgements

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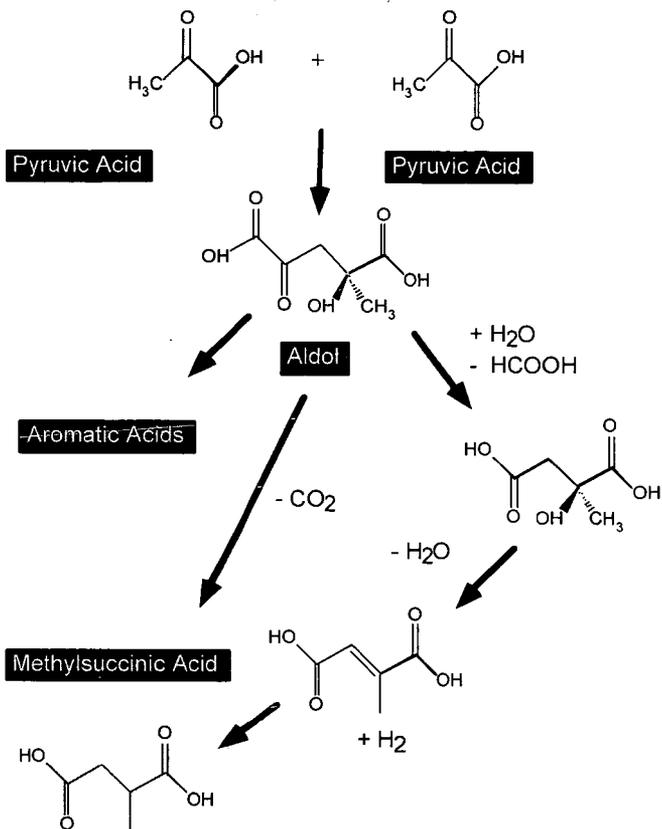


Figure 1: Reaction pathway through which pyruvic acid forms methyl succinic acid. The lack of observation of any of the intermediates suggests a concerted reaction.

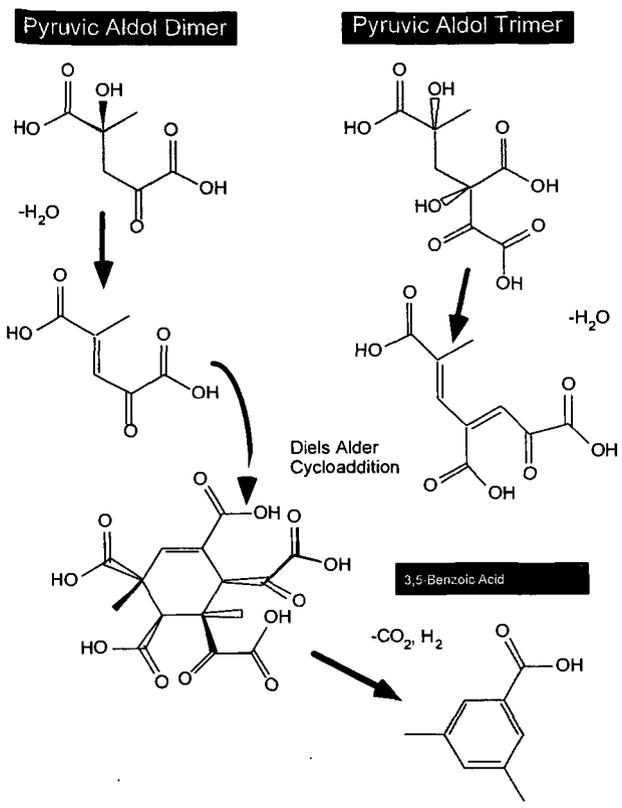


Figure 2: An example of one of many anabolic reactions exploited by pyruvic acid at elevated pressures and temperatures.

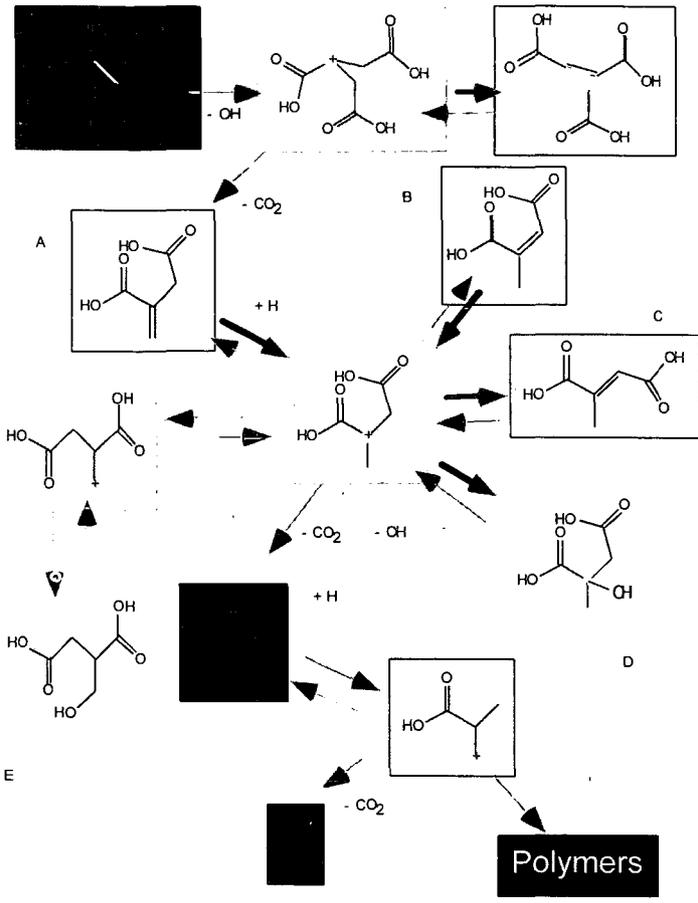


Figure 3: A schematic of the reaction network operational in the system citric acid + water at elevated temperatures and pressures.

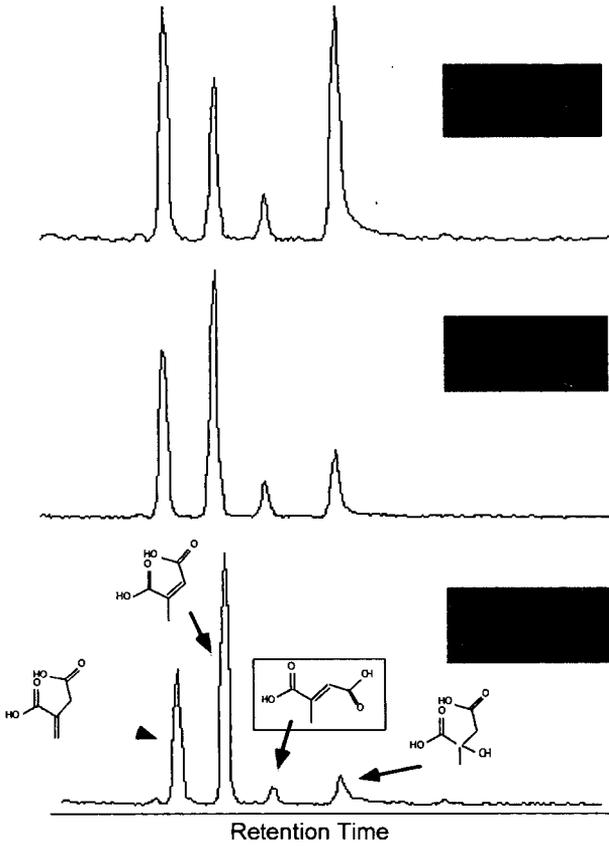


Figure 4: An example of the effect of pressure on displacing the isomeric equilibria within the system citric acid + water. Not surprisingly pressure greatly favors hydrated species.