

Hydrothermal Reactions from Sodium Hydrogen Carbonate to Phenol

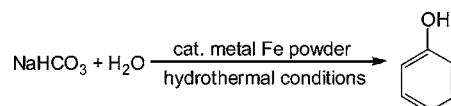
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ABSTRACT



We report here experimental evidence for the hydrothermal formation of a pure organic molecule, phenol, from the reaction of carbonate with water in the presence of iron powders.

Exploration of the origin of life is one of the most fascinating and inspiring challenges in our age.^{1–3} The basic understanding of the origin of life initiated from the hydrothermal formation of organic molecules from the primitive atmospheric compositions of CH₄, NH₃, H₂, CO₂, and H₂O.⁴ However, the information on how these organic molecules formed from the simplest inorganic molecules is still at a very beginning stage and defies clarity. Abiotic synthesis of organic compounds from CO₂ under hydrothermal conditions has been proposed as a source of the precursor compounds from which life originated.⁵ It is well-known that modern volcanic gases contain mainly H₂O and CO₂. Recent research showed that the ingredients derived from volcanic outgassing were similar to those found in modern volcanic effluent, so it might be suggested that the primitive atmosphere around the time life originated was dominated by carbon dioxide.⁶ It has been proposed that CO₂ is vented to the surface or atmosphere to be a carbon source and into the magma ocean or mantle to be sinks; the relevant sinks turned out to be carbonates such as CaCO₃ or MgCO₃ by the alteration of shallow rocks near the ambient ocean temperature.^{7,8} Sub-

sequent reactions of CaCO₃, MgCO₃, and CO₂ in the primeval water environments, producing amino acids or their fragments, must have a clear implication for the abiotic synthesis of complex organic molecules in the origin of life. On the other hand, the study on the fixation of CO₂ converting into organic compounds is regarded as one of the most expected solutions for the “Greenhouse Effect” problem.

To shed some light on the understanding of this pivotal initiative step, we studied the reactions of sodium hydrogen carbonate with water in the presence of iron powder based on the well-established mild hydrothermal method.⁹ Because sodium hydrogen carbonate can be translated into CO₂, this simulates the ocean environments of the primordial earth in a certain geological time interval.

The gas chromatography–mass spectroscopy (GC–MS) spectrum indicated that there were no detectable organic compounds in the starting purified sodium hydrogen carbonate, and the iron powder used in this experiment was also free of the contamination of the organic. Purified iron powder and sodium hydrogen carbonate were mixed with water and then added into a steel alloy autoclave (Fe–Cr–Ni alloy, GB1220-92) with a filling capacity of 90%. The mixture was then subjected to a hydrothermal treatment at 200 °C under autogenous pressure (approximate 1.8 MPa) for 5–120 h and then cooled to room temperature rapidly. The final pH

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value of the reaction solution was 9. GC–MS was employed to identify the products.

It is quite evident that phenol was formed after the hydrothermal reactions, when the mass spectrum of the product was compared to that of standard phenol (Supporting Information, Figure S1). The peak at m/z 94 is assigned to the molecular ion, $C_6H_6O^+$. Moreover, after the reaction, we found white deposition which was proved to be sodium carbonate by ICP on the bottom of the autoclave. It was noticed that the yield of phenol suddenly increases with the increase of reaction time, reaching a maximum value after 10 h, and then remains nearly constant. The yield of phenol in the hydrothermal reaction (1) is 0.8% mol according to $NaHCO_3$.



The effect of other metals and zeolites instead of iron powder under the same reaction conditions was taken into account, including Co and Ni powders, Fe_3O_4 , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} -modified ZSM-5, MCM-41, MCM-48, H- β , and Na–Y zeolites, respectively, but none of them gave considerable reactions of phenol formation, although trace amounts of phenol could be harvested with the addition of Co and Ni powders. The hydrothermal reaction in the autoclave was checked by carrying out the hydrothermal reaction in N_2 rather than in air, and we did not see an observable change either in the types of product or in the yield.

Figure 1 shows the kinetic curve for the hydrothermal

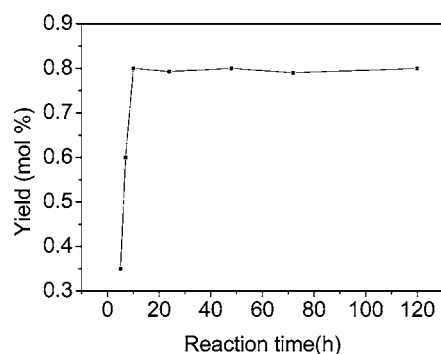


Figure 1. Kinetic curve for the hydrothermal production of phenol.

production of phenol. It is a typical self-catalysis reaction with a short induced period and fast formation reaction after the induced period. In the initial 5 h of reaction time, no organic molecules could be detected. Increasing the reaction time from 5 to 10 h, several organic molecules were identified by GC–MS, including the main product phenol and detectable amounts of formic acid and formaldehyde. The reactions completed after 10 h, and the final product was phenol only.

It has been reported that methane was discovered at an East Pacific Rise hydrothermal vent and in other crustal

fluids, which supports the occurrence of an abiogenic source of hydrocarbons.¹⁰ Usually, formation of abiogenic hydrocarbons by the reduction of carbon dioxide was thought to occur under hydrothermal conditions involving Fischer–Tropsch reactions and the serpentinization of ultramafic rocks.^{11,12} Generally, the products of this process were methanol, methane, and/or formate, which do not seem valuable for the origin of life. Organic synthesis based on CO_2 was also studied.¹³ The production of phenol from solid CO_2 reduced by Fe_3O_4 in the supercritical state was reported,¹⁴ but such reaction conditions are rigorous. Moreover, in the case of supercritical CO_2 , the excessive water was considered to be unfavorable for the formation of phenol, which is fatal for the genesis of life under hydrothermal conditions. As a possible clue to searching for the origin of life, it would be important to prove that the reactions of sodium hydrogen carbonate with water happened hydrothermally.

It is noteworthy that the reactions could take place much more efficiently under the influence of iron powder rather than cobalt and nickel under the same reaction conditions. This clearly reflects the relatively large redox potential of iron (−0.44). The result of inductively coupled plasma (ICP) of the achieved solution shows 1% of Fe ions in weight, which confirms the existence of Fe^{2+} in the reaction solution, implying the occurrence of a redox reaction. The redox reaction involved the oxidization from Fe to Fe^{2+} .

On the basis of the observation of the final product phenol and intermittent formic acid and formaldehyde in the hydrothermal reactions, we propose a possible reaction mechanism for phenol formation. Scheme 1 illustrates the main process of the hydrothermal reactions (see details in Supporting Information, Scheme S1). At the first stage of the reactions, sodium hydrogen carbonate was converted to CO_2 via its decomposition in hydrothermal solution. Subsequently, CO_2 and/or CO_3^{2-} were adsorbed and bound at the surface of metal iron. Meanwhile, metal iron reacted with water, giving H_2 and Fe^{2+} . At the surface of iron powder, CO_2 could be activated to form formaldehyde (CH_2O) finally with the attack of H_2 . The processes seem complicated but basically involve two simple types of reactions: the oxidative coupling reactions (denoted as ①) and rearrangement reactions (denoted as ②). We realized that the process of hydrogen production is the rate-determining step in the acceleration of the reactions because the reaction proceeds rapidly as soon as hydrogen is formed from the reaction of the metal iron with water. The fact that we caught trace formic acid and formaldehyde in the initial stage of the reaction confirms the suggested mechanisms. Water as the source of hydrogen is necessary in this reaction, whereas the ratio of $NaHCO_3$ to water seems to have little effect on the reduction of carbon dioxide. From our accumulated

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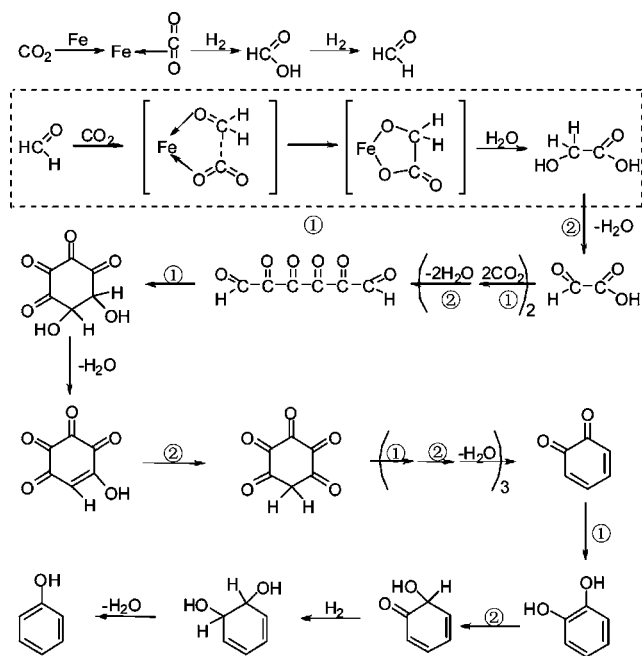
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Scheme 1. Proposed Mechanism of Phenol Formation



experimental data, we may answer a key question: the abiotic synthesis of organic compounds from CO_2 under hydrothermal conditions can serve as a source of the precursor compounds from which life originated.

It was apparently predicted that the final basic solution ($\text{pH} = 9$) restricted the further reaction to form phenol because of the smaller conversion of CO_2 and production of H_2 in basic solution, in principle. According to our proposed mechanisms, we conducted the experiment in acidic solution where enough CO_2 and H_2 were allowed. Results showed that the yield of phenol dramatically increases. This experiment confirms our mechanisms and may also provide industrial possibilities.

Our study on the hydrothermal reactions from sodium hydrogen carbonate to phenol makes it possible to form prebiotic organic molecules based on carbonate under mild hydrothermal conditions. Because of the hydrothermal formation of phenol which is a fragment of tyrosine, we understand that the existence of important small molecules such as formic acid and formaldehyde in the process of the reactions is basically the source for the hydrothermal formation of amino acids and peptides. One may believe that some of the possible subsequent reactions toward more complicated biomolecules would be expected.

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Supporting Information Available: Experimental procedure, GC–MS characterization, and the formation mechanisms of phenol. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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