Reduction of Carbon Dioxide by Magnetite: Implications for the Primordial Synthesis of Organic Molecules

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The compositions and surface pressures of the early atmospheres of Earth and Mars after the end of the heavy bombardment are still unknown. Miller has simulated electric discharges in a reducing atmosphere of CH_4, NH_3, and H_2O and obtained an aqueous solution of simple carboxylic and amino acids, which has long been considered as one of the pillars of the theory of a heterotrophic origin of life in a prebiotic broth.[1] With the allowance for exogenous sources, reducing atmospheres yield organic mixing ratios in the early oceans some 3 orders of magnitude higher than those obtained for nonreducing atmospheres.[2] Thus, models for earth's primitive atmosphere that postulate no significant abundance of reduced gases suffer the drawback that the origin of life is more difficult to understand.[3] C. Huber et al. have reacted CH_3SH and CO in the presence of FeS, CoS, or NiS in water at 100 °C, and were able to detect the formation of organic molecules.[4] Thus, an alternative theory for the origin of life being of a chemoautotrophic nature is based on these observations.[5,6] Actually, the reactants used by C. Huber et al. are still in a reduced state. Currently, the prebiotic significance of all these experiments appears to be questionable because atmospheres with less or even nonreducing properties are now favored.[7−9] However, so far no evidence has been presented that significant amounts of organic molecules related with life can be generated in an oxidizing atmosphere. It is currently suggested that the primordial atmosphere comprises mostly an unproductive mixture of CO_2, N_2, and H_2O, with CO_2 being in a dense state.[4,10] The conditions typical of crust and oceanic hydrothermal systems combine temperatures between 300 and 800 °C with pressures of 0.1−0.4 GPa, and notably magnetite is a major form of iron oxide in the present-day crust.[11] For a better understanding of the origin of life in an oxidizing atmosphere it will be important to show that carboxylic acids can indeed be formed directly from CO_2 under typical crust conditions. In view of these considerations, we have showed the reaction of dense CO_2 with Fe_3O_4 in the presence of different amounts of water. The reactants were loaded into a flexible Au/Ti reaction cell which was sealed and transferred into a steel alloy autoclave. Two capillary tubes extending from the cell permitted the attachment of a pressure-meter (if necessary) and of sampling ports for gaseous products, respectively. The Fe_3O_4 employed in this study was pure synthetic magnetite, which was characterized by X-ray diffraction (XRD) analysis before and after the reaction. With small amounts of H_2O present in the reaction mixture organic compounds including acetic acid are formed. Acetic acid and all other products were identified by gas chromatography−mass spectroscopy (GC−MS) and quantified by gas chromatography (GC). The temperature was varied to generate a range of conditions between 100 and 350 °C. The pressure was autogenic, depending on reaction conditions. In the following discussions, if it is not specifically mentioned, most of the reactions were conducted at 350 °C, 10 atm for 2.5 h.

Under the most reducing conditions, the main products which were identified included acetaldehyde, ethanol, and acetic acid (Figure 1) with small amounts of 2-butenal, hexanedial, and others being present as well. At 350 °C and 10 atm up to 4 mol % acetic acid (with respect to the initial amount of CO_2) were obtained from the reduction of CO_2 in the presence of 2 mol % H_2O (respect to the total system) (Figure 2). Interestingly, the amount of acetic acid decreases as the temperature is decreasing, while the amount of ethanol increases. No organic molecules could be detected at 125 °C, even under higher pressures (e.g., 20 atm) of CO_2 and in the presence of less H_2O. No molecular hydrogen, methane or methanol could be detected by GC−MS, indicating that the mechanism of the CO_2 reduction is quite different from that of the methanization of CO_2 by olivine,[12] involving the pregeneration of H_2. Carbon dioxide is a low-energy molecule, with the standard oxidation potential of the $CO_2/CO_2^{\bullet-}$ couple in an aprotic solvent such as N, N′-dimethylformamide (DMF) containing a non ion-pairing countercation (Net_4^+) (tetraethylammonium) being indeed as negative as −2.2V vs SCE.[14] The potential for the Fe^{3+}/Fe^{2+} redox couple is not as negative as that for the CO_2 reduction to $CO_2^{\bullet-}$, evincing that the formation of the $CO_2^{\bullet-}$ radical anion is indeed highly unlikely in the system investigated here. Furthermore, no single carbon-bearing hydrocarbon compound could be detected, suggesting that the mechanism of the observed formation of organic molecules involves a multielectron reductive coupling of a pair of carbonyls to produce an intermediate bound to the surface of the solid Fe_3O_4 particles containing ferrous ions. The XRD patterns of the solid products show the coexistence of Fe_3O_4 and Fe_2O_3 after the reaction, even when excess CO_2 had been present (CO_2:Fe_3O_4 = 5) in the reaction system. This can only be explained that the surface layer of Fe_3O_4 is oxidized to Fe_2O_3 by carbon dioxide, indicating the involvement of a surface mediated reaction. Incidentally, surface-mediated processes are often highly stereoselective, which may explain the preference of living systems for L-amino acids.[13] No ilmenite was detected by XRD analysis, which might be formed by the reaction of magnetite with Ti from gold tube. A possible reason for this is that Au/Ti alloy is stable in our reaction conditions.

To further examine the effect of water, experiments were conducted in atmospheres in which magnetite (Fe_3O_4) and different amounts of water were used. Small amounts of H_2O were found to be favorable for the reduction of CO_2 (Figure 2), while, with excess H_2O present, only trace amounts of CO_2 were reduced, yielding organic compounds (Figure 2). To test the stability of the organic compounds formed, we also carried out an experiment with a 2:1 CO_2:O_2 mixture, which showed that O_2 has no significant influence on the formation of organic com-

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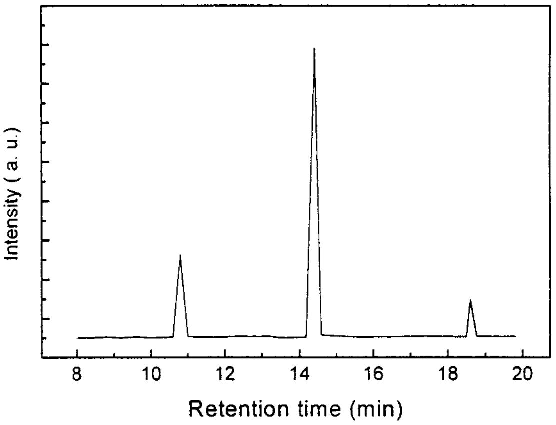

Figure 1. Ion Chromatograms of the GC−MS analysis. The reduction was conducted in $CO_2/H_2O/Fe_3O_4$ system at 350 °C, under 10 atm for 2.5 h. The peaks at 10.880, 14.324, 19.146 min correspond to acetaldehyde, ethanol, and acetic acid, respectively.

pounds. This result also implys that excess H_2O is unfavorable for the CO_2 reduction cannot simply be explained by a variation in the oxidizing condition, but the presence of excess water might rather be unfavorable for the adsorption of CO_2 on the surface of Fe_3O_4 particles (i.e., competitive adsorption).

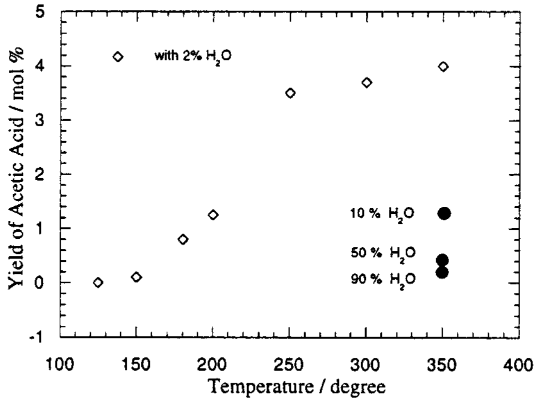

Figure 2. CO_2 reduction to CH_3COOH (given in mol %) plotted against temperature at 10 atm in $CO_2/H_2O/Fe_3O_4$ system (◇). All reactions were conducted a 2.5 h period. No detectable organic molecules were obtained in experiments conducted at 125 °C. Also shown are yields at 350 °C with different amounts of H_2O (given in mol %) added to the CO_2/Fe_3O_4 system (●).

Most gas compositions in metamorphic systems have ratios of H_2O to the total amount of gas of 0.5 or greater.[15] On the other hand, gases trapped in some mid-ocean ride basalts exhibit low ratios of H_2O to total gas.[11] Thus, CO_2 reduction to organic compounds would be restricted to such localized regions from which H_2O had been removed by processes such as chemical reactions.[9,12] Brandes et al.[16] have employed reduced iron oxides, in their experiments, demonstrating the mineral-catalyzed reduction of molecular nitrogen and nitrogen oxides to ammonia at temperatures between 300 and 800 °C. In good agreement with the Fe_3O_4/H_2O system, N_2 reduction was strongly inhibited by the presence of excess water, which is quite similar to the suppression of the acetic acid formation in our case. The activation of amino acids and the formation of peptides under primordial conditions is one of the great riddles of the origin of life. Although the activation of amino acids and the formation of peptides under hot, anaerobic, aqueous conditions is possible,[17] it is thermodynamically more favorable to form peptides from individual amino acids in a system lacking H_2O than that in its presence, in good agreement with the preferred conditions for the formation of acetic acid or ammonia, respectively.

From this study, it can first be concluded that thermal dense carbon dioxide systems are indeed attractive sites for the origin of life. Such systems contain a CO_2 reservoir, N_2, and small amounts of H_2O in the presence of reducing agents. Actually, this kind of system has been found in some mid-ocean ridge basalts.[12] Possibly, peptides were originally formed in such a system and subsequently delivered to the open ocean by CO_2 thermal or hydrothermal vent systems described in ref 18.

Second, the reduction of CO_2 may occur later than that of N_2 in the evolution of the biosphere. It has been reported that the reduction of N_2 requires high pressures and high temperatures (0.1 Gpa, 300−800 °C), which are more vigorous conditions than those required for the C−C formation from CO_2 in our case. It thus seems that CO_2 could be reduced whenever N_2 is reduced, but higher temperatures (e.g., 800 °C) would destroy rather than create organic compounds.[19]

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