Hot Stones or Cold Soup? New Investigations on the Endogenous Origin of Organic Compounds on Earth

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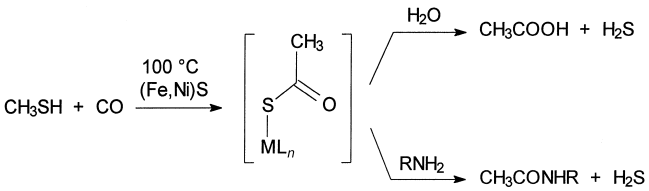
Understanding the origin of life is one of the big intellectual and experimental challenges of our time. Although there is no lack of hypotheses about this topic a generally accepted theory is presently not available. Agreement starts and stops with the fact that life on earth has existed for at least 3.5 billion years[1] and that organic molecules were required for its emergence. But how did these molecules form? Important new investigations about the origin of the building blocks of life are presented in this highlight.

The most famous experiment in this context was carried out almost fifty years ago by Stanley L. Miller, at that time a PhD student in the group of Harold Urey in Chicago.[2] Miller was able to show that electric discharges in an atmosphere of methane, ammonia, hydrogen, and water led to the formation of significant amounts of various amino acids. Experiments of this kind were repeated in numerous variants. If reducing gases were employed mixtures of organic compounds of low molecular weight could be detected in many cases. This has led to the popular idea that the primordial ocean resembled a nutritious soup.

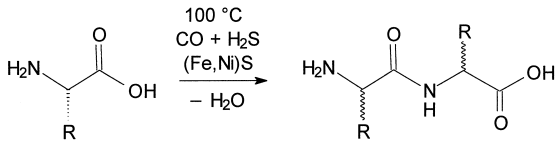
But the possibility that earth once had a reducing atmosphere is questioned. A well known argument against it is the high photolability of methane and ammonia. Because a shielding layer of ozone was missing a high concentration of these gases is believed to be unlikely. Furthermore, several other results point to a neutral atmosphere of CO_2 and N_2. Given the fact that the atmosphere was based on an unproductive mixture of CO_2 and N_2 the nutritional value of the primordial ocean drops significantly.[3]

An alternative scenario has been propagated for several years by Wächterhäuser. Instead of a primordial soup he favors hot minerals as the place where organic molecules were initially built and life subsequently emerged. Especially sulfur-containing minerals like pyrite[4] are proposed to have acted as an energy source and catalyst both under the extreme conditions found in hydrothermal or volcanic vents. Two new experimental studies by Huber and Wächterhäuser have attracted considerable interest, in which chemical model reactions supporting the above hypothesis are described. First they were able to show that in an aqueous suspension of (Fe,Ni)S at 100 °C CH_3SH and CO react to form acetic acid.[5] As an intermediate they postulate a metal-bonded thioacetate, which was detected by trapping reactions with amines (Scheme 1).



Scheme 1. Synthesis of activated acetic acid by carbon fixation of CO in the presence of (Fe,Ni)S. M = Fe, Ni.

In a subsequent study it was reported that under similar conditions (100 °C, Fe/NiS, CO, H_2S or CH_3SH) amino acids are converted to (racemic) dipeptides (Scheme 2).[6] This result is remarkable because the hydrolysis of peptides is thermodynamically strongly favored. Several exergonic reactions of CO are discussed which could provide the energy for the condensation.



Scheme 2. Condensation of amino acids at the surface of (Fe,Ni)S in the presence of CO and H_2S. R = H, CH_2Ph, $CH_2C_6H_4OH$.

After carbon fixation of CO under potentially prebiotic conditions had been realized in the laboratory, Chen and Bahnemann have recently shown that in the presence of magnetite CO_2 can be converted into organic substances.[7] In a ternary mixture of CO_2, water, and Fe_3O_4 at 350 °C and 10 bar they were able to detect acetaldehyde, ethanol, and acetic acid (up to 4%) after a few hours (Scheme 3). The extreme conditions simulate the environment of the earth's crust. The reaction, which is inhibited by larger amounts of water, can even be performed in the presence of oxygen. Thus, the range of temperatures and redox conditions over which

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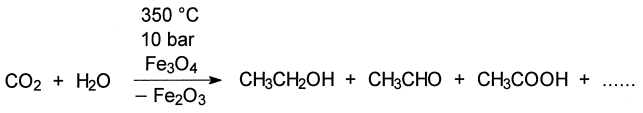

Scheme 3. Carbon fixation of CO_2 in the presence of magnetite.

organic compounds can be produced from inorganic gases is significantly expanded. Given the fact that iron oxides are common in the crust, this could be a more important source for organic substances than was previously thought.

The work described above proves that a prebiotic organic chemistry with CO and CO_2 as C_1 building blocks could have occurred in hydrothermal or volcanic settings. Remarkably, even chemically inert N_2 can be converted under such conditions. This was shown by Brandes et al.[8] Likewise with the help of magnetite the reduction of N_2, NO_2^-, and NO_3^- to NH_3 is possible at elevated temperatures (300–800 °C) and pressures (0.1–0.4 GPa). In the presence of pyrite instead of magnetite the reduction of NO_2^- and NO_3^- is even faster. This shows that certain areas of the crust as well as hydrothermal vents represent a possible source for NH_3, a molecule with relevance for the production of amino acids as described above. Given that the ammonia produced this way finally makes its way into the atmosphere, a connection between the chemistry at hot minerals and the chemistry of a primordial soup begins to emerge.[9]

Exogenous sources for organic molecules have also been discussed extensively.[3, 10] Nevertheless, compounds with extraterrestrial origin have to have been produced sometime somewhere. Possibly, the underlying chemical reactions are the same as on earth. In this case, the model reactions described above are also important for a deeper understanding.

The prebiotic synthesis of organic molecules of low complexity was an important first step for the origin of life. In view of the results presented the origin of these compounds appears to be less mysterious. But crucial further steps have not (or insufficiently) been simulated in the laboratory so far. How were long information-carrying biopolymers produced although the hydrolysis of such compounds is fast on the geological time scale? Did minerals[11] or metal ions[12] act as a catalyst? How and at which stage did the break of symmetry occur, which is manifested in the homochirality of present day biomolecules?[10, 13] And what were the first molecules which were able to self-replicate[14] and which were subsequently subjected to molecular evolution? There is plenty of room for new hypotheses and especially for new experiments.

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New and Selective Transition Metal Catalyzed Reactions of Allenes

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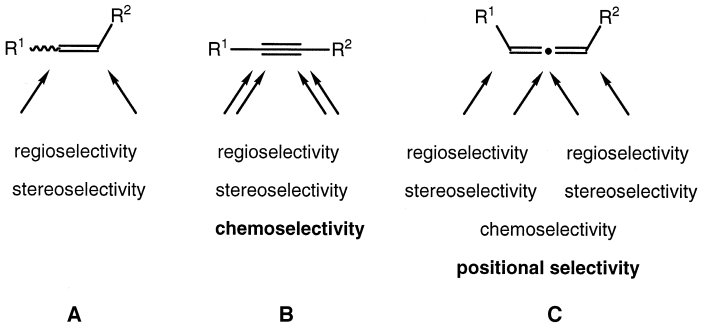
Among the most popular organic substrates for transition metal catalyzed reactions are alkenes **A** and alkynes **B** (Scheme 1). Allenes **C** have received much less attention. This is easily explained by increasing selectivity problems when we proceed from **A** to **C**. While in **A** we face the question of regioselectivity (Markovnikov versus anti-Markovnikov ori-



Scheme 1. Selectivity problems in different types of unsaturated substrates **A**–**C**.

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