sophisticated treatments with more powerful computers (*10*). So, perhaps the ball (proton) is now in the theoretical court.

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PREBIOTIC CHEMISTRY

Where Smokers Rule

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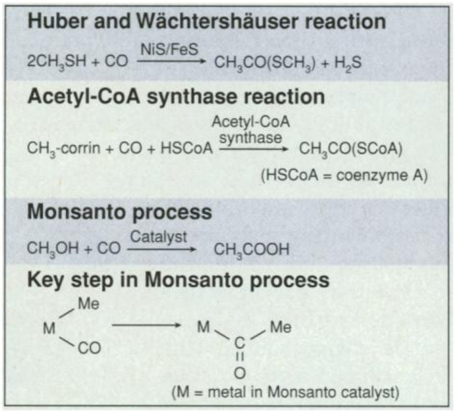
Deducing the mechanism of the origin of life on Earth (*1, 2*) has always remained a fascinating but unsolved puzzle. Some have even considered it too difficult for scientific study, because the direct evidence is long gone and we can only work by plausible inference. Although this is indeed a very difficult problem to approach experimentally, a number of striking observations over the years have allowed the formulation of plausible scenarios for the prebiotic synthesis of various important biomolecules. The report by Huber and Wächtershäuser on page 245 of this issue (*3*) directs our attention to the possibilities (*4*) afforded by the unusual chemistry (*5*) of deep sea vents.



In a celebrated experiment (*1*) by Miller, a mixture of hydrogen, methane, ammonia, and water, a then-plausible imitation of the early Earth atmosphere and ocean, was exposed to electric discharges, much as this early chemical mixture might have been exposed to lightning, to produce several amino acids in significant amounts. Purines and pyrimidines were obtained from hydrogen cyanide and cyanoacetylene under similar conditions. Organic molecules formed in this or other ways are considered to give rise to a "primordial soup" that may have provided favorable conditions for the origin and development of life. Subsequent revisions of the probable composition of the early Earth atmosphere (hydrogen, for instance, may not have been an important constituent) have clouded the interpretation of the experiment.

In the deep ocean, hydrothermal vents can discharge a cocktail of chemicals, including hydrogen sulfide and related species and a dark "smoke" of metal sulfides—hence, the term "black smokers." Today, these locations shelter a group of unusual biota that depend on these volcanic discharges for their energy supply.

Most scenarios for the origin of life involve processes that might occur in surface waters or in shallow seas. Huber and Wächtershäuser have instead favored the possibility (*4*) that the exotic environment of the deep-sea vents might be favorable for the origin of life. They have shown that mixed iron nickel sulfides act as a catalyst for the conversion of methyl thiol and carbon monoxide, present in vent gases, to methyl thioacetate, $CH_3CO(SCH_3)$, a compound with a C-C bond and containing an activated acetyl group (see figure). This compound resembles acetyl–coenzyme A (acetyl-CoA), or $CH_3CO(SCoA)$, a central intermediate in the biosynthesis of a variety of important biomolecules. The abiological C-C bond–forming reaction of Huber and Wächtershäuser can therefore be seen as a plausible preliminary step in the building up of more complex organic molecules in or near the early Earth vents.

The hypothesis that metal sulfides could play a prebiotic catalytic role is attractive because nature uses Fe_4S_4 and Fe_2S_2 groups, essentially fragments of the iron sulfide lattice, as the catalytic sites in many enzymes found in all types of organisms today (*6*). Nickel-iron-sulfur sites, though much rarer, most notably occur (*7*) in acetyl-CoA synthase and other enzymes present in a group of evolutionarily primitive organisms, the archaebacteria (*8*), which show a number of biochemical peculiarities that distinguish them from other organisms. In particular, acetyl-CoA synthesis occurs in some of these organisms from CoASH, methylcorrin, and CO (figure), a reaction catalyzed by a Ni-Fe-S cluster of still undetermined structure in the Ni-Fe-S enzyme acetyl-CoA synthase (*9*).

The mechanism of the reactions discussed above is uncertain, but a clue is afforded by an important industrial process, first developed by Monsanto Company, for which the mechanism is well known (*10*). In this metal-catalyzed process, CH_3OH reacts with CO to give CH_3COOH via the intermediates shown in the figure. The key C-C bond–forming step, a migration of a methyl group to a coordinated CO, is the most likely pathway for the newly proposed reaction.

The results raise interesting questions. Could the acetyl-CoA synthase pathway be a biochemical fossil, not only from the first organisms, but also from the prebiotic pathway that produced activated acetyl fragments, the prebiotic equivalents of acetyl-CoA? Is the presence of life in subsurface water deposits a possibility even when a planet has an inhospitable surface?

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