Carbonyl sulfide–mediated prebiotic formation of peptides: irrelevant for origin of life purposes

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On 19 May 2023, Christian Professor James Tour and Mr Dave Farina, a prominent atheist and YouTuber, held a debate at Rice University on the topic, "Are we clueless about the origin of life?"[1] The event has drawn considerable attention on the internet since Farina, who goes by 'Prof. Dave', has exploited a multi-million market of followers who delight in abusing Intelligent Design and creation science personnel in a trademark acrimonious manner that fails to address the science.

During the debate, Farina constantly alleged there was 'tons of research' supporting his contentions. This was followed up within hours by an attendee at the debate who posted a YouTube video on a paper by Orgel and Ghadari from 2004.[2,3]

This video, titled *Debunking James Tour on the Origin of Life*, has been widely linked to other YouTube channels including by Farina. Many science novices promptly began joyfully heaping triumphant abuse in the comment sections on Professor Tour, safe in the knowledge that he had no possibility of responding to each pellet from all the shotgun salvos aimed at him.

However, in the referenced paper, Leman, Orgel and Ghadiri did not claim that their experiments reflected a prebiotic relevant scenario, instead writing cautiously about carbonyl sulfide (COS):

> "We speculated that COS might have played a more general role as a condensing agent in prebiotic chemistry."[2]

Professor Tour sets the trap.

During the debate, Tour repeatedly offered his partner a piece of chalk and asked him to "show the chemistry". He also stated, repeatedly, that Farina should stop quoting hyped-up titles and abstracts and needed to analyze what was done experimentally.

Steve Grayson accepted the first request in a YouTube video.[3] By providing a reference with the chemistry we can now engage in some real scientific discussion. That was the first mistake. Professor Tour's second piece of advice, to analyze what was done experimentally, was overlooked by Grayson, who otherwise has posted some interesting videos on non-scientific topics.[3] The experiments performed were not even mentioned in the video, far less discussed for prebiotic plausibility.

Grayson has engaged in several online debates and seems like a very reasonable and fair person so I will now clarify for him and others what they must not overlook.

It is instructive to review the actual experiments since a recurrent principle is revealed. What we read in the abiogenesis chemistry literature has nothing to do with abiogenesis *research*. It is merely laboratory chemistry, optimized to obtain the wished for results.

What does this claim mean? The goal of the abiogenesis community is to find a natural explanation for how cellular life arose through natural processes. So, what is being *researched*? The chemistry of ancient sedimentary rocks? Or is cellular biochemistry being analyzed in an attempt to work backwards? Certainly not. Organic chemistry specialists are applying advanced knowledge of how various chemical products could be derived in a laboratory, investing considerable effort to optimize the conditions in order to get the intended result. At most, there are sometimes some lame, unsubstantiated *post facto* claims for why their work might be relevant for origin of life (OoL) purposes.

We have no issue with the laboratory chemistry. Where we take issue is with the *a priori* and clearly absurd claims that some particular OoL problem has been thereby resolved. In a scientific discussion, everyone should object to this.

The experiment

Pure L-phenylalanine amino acid was reacted with pure carbonyl sulfide (COS), leading to an intramolecular cyclization intermediate α-amino acid *N*-carboxyanhydride (NCA). This then reacted with a second L-phenylalanine to produce a dipeptide in 6.8% yield, as shown in figure 1.

During the debate, Tour had emphasized that the amino acids form zwitterions in aqueous solutions having a very low free energy, making them unreactive. An audience participant had asked Farina if any of the papers he referred to included amino acids which had not been derivatized to prevent forming zwitterions. Farina assured her this was so. This answer was obviously nonsense, and, needless to say, we also see that molecule 2 in figure 1 is not a free amino acid.

The experiment is irrelevant for OoL purposes.

The following facts show why the reported work does not demonstrate how large polypeptides could have naturally formed in water.

1. In volcanic plumes, COS is a trace gas present in a ratio of 1000–10,000:1 CO_2:COS.[4] COS has a lifetime in the atmosphere of about around 7 years and is currently found in the range 0.51–0.53 parts per billion volume ratio (ppbv).[5] However, this includes all the emissions from chemical processes and the output from plant material. Amino acids like phenylalanine, the companion reactant, are not released by volcanos. OoL specialist Bada estimated that the maximum concentration of amino acids in ancient oceans would have been only about 10^{-8} g/l, which corresponds to about 10^{-10} M.[6]
2. Furthermore, phenylalanine and COS must both be co-located to react and form the intermediate NCA. (The authors did not explain why phenylalanine was selected, and no results for other amino acids were provided.)
3. Therefore, to obtain NCA in a laboratory, the chemists used a COS concentration of 400×10^{-3} M and 50×10^{-6} M for phenylalanine—artificial and impossible enhancements of ~100,000 times![2] For prebiotic modelling purposes that is absurd, especially when we reflect a little deeper.

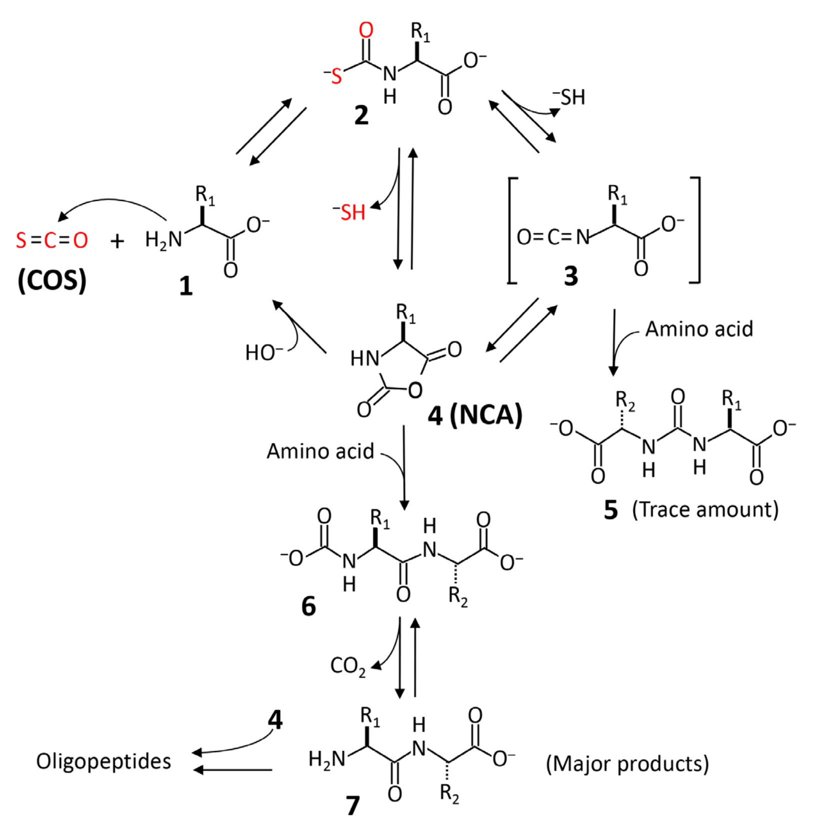

Figure 1. Reaction scheme to produce a dipeptide (after Leman *et al.*[2])

4. COS, a *gas*, reacts quickly with water to form hydrogen sulfide (H_2S) and carbon dioxide (CO_2).[7] Therefore, the concentrations actually dissolved in a huge prebiotic ocean would have been unmeasurably small. So how did the chemists resolve this problem?
   First, the experiments were performed in a 25-ml Schlenk tube, preventing the reactants from diffusing away.
   Then, *pure COS gas was forced (bubbled) into the reaction mixture!* Right next to the extremely pure, concentrated phenylalanine. What does this have to do with prebiotic chemistry? Nothing! Furthermore, the reported experiment used 8 times more moles of COS than phenylalanine, to optimize the outcome (at least for the outcome they sought).

5. The high concentrations were also necessary so that the intermediate NCA formed would be forced to react with a second phenylalanine.
6. There is another reason why the absurdly high concentration of reactants was necessary: the key intermediate, *NCA, is unstable in water with a half-life of only ~10 hours* in their setup.[2] Under realistic abiotic conditions, NCA would essentially never have encountered and reacted with another phenylalanine. Especially when we take pH into account.
7. Furthermore, volcanic vapours are acidic. For example, detailed studies on plume from the Erebus volcano identified the very strong acids HCl, HF, HNO_3 (>0.03 ppbv), and H_2SO_4 (~0.4 pptv).[8] Therefore, to prevent the destruction of COS and NCA the researchers deliberately worked under very *basic* conditions (initial pH = 9.6). To achieve this a CHES (2- (cyclohexylamino) ethane sulfonic acid) buffer was used, not just irrelevant for prebiotic 'research' but yet another outrageous artifice for OoL proponents to ignore.

   Figure S2 of the Supporting Online Material shows that lowering the pH to just 7.7 decreased the yield of dipeptide by a factor of about 15 to almost 0%! In fact, a higher pH of 10.5 also led to a comparable drop in dipeptide yield suggesting a narrow, required pH range—well outside of that which the alleged volcanic condensate would have.

   This illustrates *the considerable effort invested by the researchers to find the ideal laboratory conditions*, and the results from these experiments were then published.
8. Destruction by acid catalysis cannot simply be ignored. The authors wrote:

   "Because the gas hydrolyzes rapidly on a geological time scale, it is unlikely to have accumulated to a high concentration in the atmosphere. Thus, if COS was important in prebiotic chemistry, it is likely to have functioned *in localized regions close to its volcanic sources*."[2]

   But close to its volcanic sources would mean next to all the destructive acid from the volcanos. A pH of ~9.6 is absurd for OoL purposes. The authors did not report what the half-life of NCA would be at, for example, a pH < 5.

   Incidentally, Grayson also claims that hydrothermal vents would have been a suitable environment for origin of life purposes, such as during a debate on May 25, 2023.[9] However, at a lower temperature of c. 25°C (to minimize the destructive hydrolysis of peptide bonds) hydrothermal fluids have values of pH ≈ 4.7 – 5.4.[10,11]
9. After all the considerable, highly intelligent optimizations had been applied, a meager dipeptide yield of 6.8% was obtained. Lowering both reactant concentrations by many, many orders of magnitude would show that any peptide formed would be too dilute to measure in an ocean, especially since it would hydrolyze much faster than new peptides could form.

   Furthermore, and most unfortunately for evolutionists, a vast number of polypeptides >100 residues would be needed for biogenesis purposes, not simple dipeptides. The fact that these would also racemize was also not mentioned.[12]
10. The researchers meticulously excluded all the other molecules (which would have been present in high concentrations), which would have reacted with COS and NCA, hindering dipeptide formation.

Conclusion

Another chemical laboratory pathway was described to produce a dipeptide after derivatizing the reactant amino acid. Enough laboratory methods to accomplish this are already known which produce higher than 6.8% yield. The described conditions have no relevance to a putative prebiotic world and no effort was made to adjust the parameters to permit extrapolations to calculate realistic dipeptide concentrations or reaction times. Both the intermediate NCA and dipeptide would have hydrolyzed much faster than new dipeptide could have formed.

References

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