

# IS CYANOACETYLENE PREBIOTIC?

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**Abstract.** Cyanoacetylene is an earlier intermediate in a proposed prebiotic synthesis of cytosine, while cyanoacetaldehyde is a later intermediate. There is no scientific basis for the claim that cyanoacetaldehyde is more plausibly prebiotic than cyanoacetylene in this context.

**Keywords:** cyanoacetylene, cyanoacetaldehyde, cytosine, prebiotic synthesis

## 1. Background

In 1966, Sanchez, Ferris and Orgel in a report in *Science* (Sanchez *et al.*, 1966), described the isolation of cyanoacetylene from a spark discharge reaction in a methane-nitrogen mixture. They went on to show that cyanoacetylene reacts with 1 M sodium cyanate in aqueous solution to give cytosine in up to 5% yield, and suggested that this reaction sequence might be relevant to the origin of life. In a later paper (Ferris *et al.*, 1968) they continued to emphasize the prebiotic relevance of this reaction but also reported briefly the closely related synthesis of cytosine in 4.8% yield from cyanoacetylene and 1 M urea. In the same paper they demonstrated the hydrolysis of cyanoacetylene to cyanoacetaldehyde. They expressed no view on the mechanism of the reaction of cyanoacetylene with urea.

In 1974, Ferris, Zamek, Altbuch and Freiman returned to the topic of pyrimidine synthesis (Ferris *et al.*, 1974). They hypothesized that cyanoacetaldehyde was an intermediate in the synthesis of cytosine from cyanoacetylene but were unable to detect cytosine as a product from a reaction involving cyanoacetaldehyde and 0.1 M urea. They did, however, isolate 2-4-diaminopyrimidine in about 3.5% yield in a reaction of cyanoacetaldehyde (or cyanoacetylene) with 0.2 M guanidine.

Beginning in 1995, Miller and his colleagues have re-investigated the reactions of cyanoacetaldehyde. In particular, Robertson and Miller showed that cyanoacetaldehyde reacts with a saturated solution of urea (about 18 molal) to give cytosine in up to 50% yield, and have claimed that this reaction is prebiotic (Robertson and Miller, 1995a). When they used 1 M urea they obtained a yield of about 3%, reasonably close to the yield (4.8%) obtained by Sanchez, Ferris and Orgel starting with cyanoacetylene. The similarity of the chemistry involved was commented on by Robertson and Miller in a correction to their original paper, in which the earlier results had been overlooked (Robertson and Miller, 1995b).



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## 2. Cyanoacetylene or Cyanoacetaldehyde as the Prebiotic Precursor of Cytosine?

In a very recent publication in *Origins of Life and Evolution of the Biosphere*, Nelson *et al.* (2001) argue that cyanoacetaldehyde is a prebiotic molecule and that cyanoacetylene is not. I believe that they have confused issues of mechanism with issues of 'prebioticity', and that their claim is, therefore, untenable.

The facts are not in dispute. Cyanoacetylene can be obtained by sparking a methane-nitrogen mixture. Cyanoacetylene hydrolyzes readily to cyanoacetaldehyde. Cyanoacetaldehyde reacts with urea to give cytosine. No prebiotic synthesis of cyanoacetaldehyde other than from cyanoacetylene has been demonstrated. Cyanoacetylene is, therefore, an earlier intermediate in the proposed prebiotic synthesis of cytosine from an atmosphere of methane and nitrogen and a solution of urea, while cyanoacetaldehyde is a later intermediate.

The reasons for accepting or rejecting reagents or reactions as prebiotic are obviously complex, but a general discussion of them would be beyond the scope of this comment. In the particular case of cytosine synthesis, there is clearly no scientific reason for rejecting cyanoacetylene and accepting cyanoacetaldehyde as a prebiotic source of cytosine (or vice versa). This is largely a semantic issue, but I believe that it is a significant one, because it is important for the field of prebiotic chemistry to distinguish clearly between the discovery of new syntheses, the elucidation of their mechanisms and the proposal of scenarios that might make them relevant to the origin of life.

In conclusion, I would like to make two further points that are peripheral to the main argument. First, Miller and his coworkers have suggested, without providing any experimental evidence, that there may be an alternative prebiotic route to cyanoacetaldehyde (Nelson *et al.*, 2001). Evidence for such a reaction would be interesting, but would not eliminate cyanoacetylene as a potentially prebiotic molecule. Second, the plausibility of all scenarios for the synthesis of cytosine from cyanoacetylene or cyanoacetaldehyde has been challenged vigorously (Shapiro, 1999).

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