Aldehydes and oxidant synthesized from CO_2/CO/H_2O atmospheres

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Formaldehyde (HCHO) has been known to be produced photochemically from CO in a CO_2 atmosphere. Our new experimental and theoretical studies demonstrate that HCHO production relative to CO oxidation (f) depends on total pressure and atmospheric redox state, but is not sensitive to the partial pressure of CO. In oxidizing atmospheres like those of modern Earth and Mars, oxidation of CO is far faster than HCHO production ($f << 1$), whereas in reducing early atmospheres, aldehyde synthesis from CO is significant ($f \sim 0.1$). For early Earth, the estimated global HCHO production rate is on the order of 10^{11} mol/year, assuming a CO_2-dominated atmosphere with minor CO and H_2 (Watanabe and Ozaki, 2024), which is consistent with earlier estimates (Pinto et al., 1980). Furthermore, HCHO could be converted into carbohydrates through the formose reaction on early Earth and early Mars (Ueno et al., 2024; Koyama et al., 2024). However, glycolaldehyde synthesis from HCHO (i.e., dimerization) is the bottleneck initiating the formose reaction. Here we report new systematic experiments demonstrating that not only HCHO, but also acetaldehyde, glyoxal, glyoxylate, and glycolaldehyde were synthesized simultaneously, especially when total pressure exceeds 0.1 bar in the presence of water (cloud/rain). Upon dissolution into water, these aldehydes are condensed to form sugars and other carbohydrates, and oxidized by co-produced oxidants to form sugar acids, hydroxy acids, keto acids, dicarboxylic acids, and fatty acids. Among these, certain keto acids are further decarboxylated to regenerate small aldehydes. As a result, glycolaldehyde and certain specific species are recycled through a respiration-like cyclic reaction, which may represent the first proto-metabolism, self-organized from CO_2/CO/H_2O under solar UV radiation, sustained in and adapted to the environment, and thus potentially capable of transitioning into living systems.

Keywords: Origin of Life, Atmospheric chemistry, Protometabolism, Astrobiology