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Beyond Formaldehyde: Atmospheric Synthesis from CO_2 and CO

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Solar UV photolysis of CO_2 is known to produce CO and subsequently formaldehyde (HCHO), which is important for prebiotic chemistry [1]. Recent theoretical, experimental, and isotopic studies have demonstrated that the sedimentary organic matter in early Martian sediment could be derived from the CO-mediated photochemistry in a reducing early atmosphere [2,3]. Potentially, not only HCHO, but also several other aldehydes, alcohols and organic acids could be produced from CO [4,5], however, related chemistry has not been understood enough to modeling organic synthesis in a planetary atmosphere. Here, we report the summary of our systematic experiments on UV photochemistry of CO_2 and CO atmospheres with H_2O and H_2. The quantitative GC and IC analysis and qualitative HPLC-Orbitrap MS analysis showed that various C2 compounds (mainly acetaldehyde, glycolate, and glyoxylate) were synthesized from CO in addition to HCHO and formate. Smaller amount of some C3 compounds including lactate and pyruvate were also detected. Furthermore, some of the aldehydes and carboxylic acids were formed even started from CO_2 atmosphere under the presence of H_2.The systematic analysis of the experimental results indicate that the major gateway to the C2 compound is as follows:

$CO_2 + h\nu \rightarrow CO + O$ (R1)

$CO + OH \rightarrow CO_2 + H$ (R2)

$CO + H + M \rightarrow HCO + M$ (R3)

$HCO + HCO \rightarrow HCHO + CO$ (R4a)

$HCO + HCO \rightarrow$ [C2 organics] (R4b)

Factor controlling the speciation of the product is still poorly understand, though the branching ratio of the competing reactions R4a and R4b is a key to understand production of prebiotically important molecules quantitatively. We will discuss how the total pressure and other physico-chemical parameters determines speciation and production rate of various aldehydes and organic acids though the photochemistry of CO_2 and CO atmospheres.

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[5] Zang et al. (2022) *Astrobiology* **22**, 387-398