

4.079 Carboxylic acid photochemistry is a marine source of glyoxal and other aldehydes.

Early Career Scientist

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Abstract:

Glyoxal is a highly water-soluble precursor in secondary organic aerosol (SOA) formation. Over land, glyoxal is known to be produced by the oxidation of volatile organic compounds (VOC) from both anthropogenic and natural sources. However, marine sources are still not well understood. Previous studies above the remote Pacific Ocean have detected typical glyoxal mixing ratios of 30-40 pptv, concentrations too high to be explained with current chemical understanding or atmospheric models. Because the lifetime of glyoxal is very short, the glyoxal found must have originated from, rather than been transported to, the open ocean. Furthermore, eddy covariance measurements indicate that an organic surface microlayer may be producing the glyoxal by as yet unknown processes. Here we present laboratory studies of the formation of glyoxal from carboxylic acid photochemistry. Nonanoic, octanoic, and heptanoic acids were floated on water in a quartz flow tube. Irradiation of the carboxylic acids converts them into their equivalent alkenals. The alkenals are volatile and are carried into a dark glass bottle by purified atmospheric gas. Subsequent ozonolysis of the alkenals in the glass bottle leads to the formation of glyoxal. We employ a PTR-MS to detect the alkenals, and a cavity-enhanced DOAS to detect the glyoxal. Considering the ubiquitous occurrence of carboxylic acids and their derivatives in the environment, this mechanism has the potential to be a significant source of glyoxal in the atmosphere.