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Increased stable carbon isotopic ratios of dicarboxylic acids in the Arctic aerosols during and after polar sunrise

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Stable carbon isotopic ratios ($\delta^{13}\text{C}$) of low molecular weight dicarboxylic acids and ketocarboxylic acids were measured in the Arctic aerosols collected from late winter to early summer including dark winter and polar sunrise seasons after derivatization to butyl esters and/or dibutoxy acetals using a capillary gas chromatography combined to on-line combustion/isotope ratio mass spectrometer. We found that $\delta^{13}\text{C}$ of oxalic acid (C2) increased from -23 permil in early March (before polar sunrise) to -5 permil in May (after polar sunrise). Malonic acid (C3) also showed an increase of $\delta^{13}\text{C}$ from late February (-25 permil) to May 8 (-17 permil). Glyoxylic acid (2-oxoethanoic acid), a precursor of oxalic acid, also showed similar increase from -18 permil in late February to -10 permil in May. In contrast, isotopic composition of succinic acid (-32 permil to -24 permil) did not show a systematic trend. Concentrations of oxalic acid and glyoxylic acid preferentially declined when the isotopic ratios of C2, wC2 and C3 increased. We interpret that the enrichment of ^{13}C occurred in the course of increased solar radiation during polar sunrise as a result of preferential decomposition of small diacids and ketoacid that are enriched with ^{12}C . We consider that ^{12}C - ^{12}C bond decay preferentially over ^{12}C - ^{13}C bond of oxalic and other acids during photochemical decomposition. Here, we propose that $\delta^{13}\text{C}$ of oxalic acid can be used as a tracer to evaluate photochemical aging of organic aerosols.

Keywords: Arctic, Aerosols, Water soluble organic compounds, Dicarboxylic acids, Stable carbon isotopic composition