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Photolysis of biogenic C_6 aldehydes under atmospheric conditions

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Natural or biogenic sources account for around 90% of the volatile organic compounds (VOCs) emitted into the atmosphere. As a result, biogenic VOCs play a dominant role in the chemistry of the atmospheric boundary layer and lower troposphere. One particularly important group of biogenic VOCs are the C_6 aldehydes, n-hexanal, E-2-Hexenal, Z-3-Hexenal and EE-2,4-hexadienal, which are emitted from trees, plants and shrubs and have been detected in air samples all over the world. The major atmospheric degradation processes for these compounds are expected to be photolysis by sunlight and gas-phase reaction with hydroxyl (OH) radicals, nitrate (NO_3) radicals and ozone (O_3). However there is very little data reported in the literature on the atmospheric degradation of the biogenic C_6 aldehydes.

In this work the photolysis of E-2-hexenal, Z-3-hexenal and E,E,-2,4-hexadienal, has been investigated under atmospheric conditions. Experiments were performed in an indoor simulation chamber and also at the large volume outdoor European Photoreactor in Valencia, Spain. The photolysis rates were determined from direct measurements of the decay of the compounds using GC-PID and in situ FTIR spectroscopy. UV absorption cross-section data was obtained for the 3 compounds and used to calculate maximum photolysis rates assuming a quantum yield of unity. The measured photolysis rates were compared to the maximum theoretical photolysis rates and used to derive effective quantum yields for photolysis by sunlight. Atmospheric lifetimes for photolysis were calculated and compared to the lifetimes for reaction with OH, NO_3 and O_3 to determine the relative importance of the various loss processes. Mechanisms

for photolysis are proposed and further atmospheric implications are discussed.