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Daytime tropospheric loss of hexanal and trans-2hexenal: OH kinetics and UV photolysis

E. Jiménez, B. Lanza, E. Martínez, and J. Albaladejo Departamento de Química Física, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Avda. Camilo José Cela, s/n. 13071 Ciudad Real, Spain

Abstract. The ultraviolet (λ =250–370 nm) photolysis and the OH-initiated oxidation of hexanal and trans-2-hexenal, which are relevant atmospheric processes, have been investigated at room temperature and as a function of temperature (T=263-353 K), respectively. This kinetic study as a function of temperature is reported here for the first time. Absolute absorption cross sections (σ_{λ}) were obtained using a recently built system operating in the UV region. The obtained σ_λ allowed the estimation of the photolysis rates (J) across the troposphere. Kinetic measurements of the gas-phase reaction of hydroxyl radicals (OH) with hexanal and trans-2hexenal were performed by using the laser pulsed photolysis/laser-induced fluorescence technique. Rate coefficients k_{OH} for both aldehydes were determined at temperatures between 263 and 353 K at 50 Torr in helium or argon bath gases. The temperature dependence of k_{OH} for both aldehydes was found to be slightly negative. The tropospheric lifetime of hexanal and trans-2-hexenal due to the chemical removal by OH radicals has been estimated across the troposphere. The loss rate due to the OH chemical removal was compared with the estimated photolysis rates. Our results show that OH-reaction is the main loss process for these aldehydes in the troposphere, although photolysis is not negligible for hexanal.

■ Final Revised Paper (PDF, 862 KB) ■ Supplement (75 KB) Discussion Paper (ACPD)

Citation: Jiménez, E., Lanza, B., Martínez, E., and Albaladejo, J.: Daytime tropospheric loss of hexanal and trans-2-hexenal: OH kinetics and UV photolysis, Atmos. Chem. Phys., 7, 1565-1574, 2007.
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