Geophysical Research Abstracts, Vol. 8, 08619, 2006
SRef-ID:

Rate coefficients for the reaction of OH with a series of unsaturated aldehydes between 244 K and 374 K

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Several plant species are known to emit significant quantities of volatile organic compounds (VOCs) in response to wounding. The emitted VOCs include combinations of saturated and unsaturated aldehydes, alcohols and esters. (E)-2-hexenal has been identified as a significant emission product from a variety of plants, for example grapes, plums chamise, grasses, European aspen and clover leaves. That (E)-2-hexenal is emitted by such diverse species of plants suggests a possible global importance to regional ozone production and air quality.

The daytime atmospheric loss of unsaturated aldehydes, such as (E)-2-hexenal, is largely determined by their reaction with the OH radical. The atmospheric degradation of these aldehydes will impact regional HO_X and ozone production. At present, only limited laboratory OH rate coefficient data and atmospheric degradation mechanisms are available for this potentially important class of biogenic unsaturated compounds, in particular for (E)-2-hexenal. The previously reported room temperature rate coefficient data shows significant discrepancies in the reported values. In addition, the temperature dependence of the OH + unsaturated aldehydes rate coefficients has not been reported. Therefore, further rate coefficient studies are needed.

In this work, rate coefficients for the gas-phase reaction of the OH radical with (E)-2-pentenal, (E)-2-hexenal, and (E)-2-heptenal, a series of unsaturated aldehydes, are reported. Although (E)-2-pentenal and (E)-2-heptenal are of lesser atmospheric importance than (E)-2-hexenal, measurements of their OH rate coefficients helps establish the reactivity of this class of compound. Rate coefficient measurements were made using the technique of pulsed laser photolysis with laser-induced fluorescence detection of the OH radical over the temperature range 244 K to 374 K and at pressures between 23 and 150 Torr. The measured rate coefficients are reproduced very well by the Arrhenius expressions; k_1 = (7.88 ± 1.14) $\times$ 10^{-12} exp[(508 ± 16)/T] cm^3 $molecule^{-1}$ s^{-1}, k_2= (7.48 ± 1.11) $\times$ 10^{-12} exp[(520 ± 30)/T] cm^3 $molecule^{-1}$ s^{-1}, and k_3 = (9.70 ± 1.52) $\times$ 10^{-12} exp[(450 ± 14)/T] cm^3 $molecule^{-1}$ s^{-1} for (E)-2-penetnal, (E)-2-hexenal and (E)-2-heptenal, respectively. The room temperature, 297 K, rate coefficients measured in this work (in units of 10^{-11} cm^3 $molecule^{-1}$ $s^{-1})$ are (E)-2-pentenal, (4.29 ± 0.56); (E)-2-hexenal, (4.33 ± 0.43); (E)-2-heptenal, (4.40 ± 0.66). The quoted uncertainties are 2σ and include estimated systematic errors. The present results are compared with previously published room temperature rate coefficient data and the discrepancies are discussed. The atmospheric degradation of unsaturated aldehydes is also discussed.