Studies of the gas phase reactions of linalool, 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol with O_3 and OH radicals

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The reactions of three unsaturated alcohols (linalool, 6-methyl-5-hepten-2-ol and 3-methyl-1-penten-3-ol) with ozone and OH radicals have been studied using simulation chambers at T ~ 296 K and P ~ 760 Torr. The rate coefficient values (in cm^3 $molecule^{-1}$ s^{-1}) determined for the three compounds are: linalool, $k_{O3} = (4.1 \pm 1.0) \times 10^{-16}$ and $k_{OH} = (1.7 \pm 0.3) \times 10^{-10}$; 6-methyl-5-hepten-2-ol, $k_{O3} = (3.8 \pm 1.2) \times 10^{-16}$ and $k_{OH} = (1.0 \pm 0.3) \times 10^{-10}$; 3-methyl-1-penten-3-ol, $k_{O3} = (5.2 \pm 0.6) \times 10^{-18}$ and $k_{OH} = (6.2 \pm 1.8) \times 10^{-11}$. From the kinetic data it is estimated that for the reaction of O_3 with linalool, attack at the R-CH=C(CH_3)$_2$ group represents around (93 ± 52)% ($k_{6\text{-methyl-5-hepten-2-ol}}/k_{linalool}$) of the overall reaction with reaction at the R-CH=CH_2 group accounting for about (1.3 ± 0.5)% ($k_{3\text{-methyl-1-penten-3-ol}}/k_{linalool}$). In a similar manner it has been calculated that for the reaction of OH radicals with linalool, attack of the OH radical at the R-CH=C(CH_3)$_2$ group represents around (59 ± 18)% ($k_{6\text{-methyl-5-hepten-2-ol}}/k_{linalool}$) of the total reaction while addition of OH to the R-CH=CH_2 group is estimated to be around (36 ± 6)% ($k_{3\text{-methyl-1-penten-3-ol}}/k_{linalool}$).

Analysis of the products from the reaction of O_3 with linalool confirmed that addition to the R-CH=C(CH_3)$_2$ group is the predominant reaction pathway. The presence of formaldehyde and hydroxyacetone in the reaction products together with compelling evidence for the generation of OH radicals in the system, indicates that the hydroperoxide channel is important in the loss of the biradical [(CH_3)$_2$COO]* formed in the reaction of O_3 with linalool. Studies on the reactions of O_3 with the unsaturated alcohols showed that the yields of SOA are higher in the absence of OH scavengers compared to the yields in their presence. However, even under low-NO_X concentrations, the reactions of OH radicals with 3-methyl-1-pentene-3-ol and 6-methyl-5-hepten-2-ol will make only a minor contribution to SOA formation under atmospheric conditions. Relatively high yields of SOA were observed in the reactions of OH with linalool although the initial concentrations of reactants were quite high. The importance of linalool in the formation of SOA in the atmosphere requires further investigation. The impact following releases of these unsaturated alcohols into the atmosphere are discussed.