The Effect of Functionality on the Reaction of Ozone with a Series of Oxygenated Hexene Derivatives

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Introduction

Large quantities of volatile organic compounds are emitted directly into the atmosphere from biogenic and anthropogenic sources. On a global basis, it is estimated that biogenic volatile organic compounds (BVOCs) account for 50% of hydrocarbon emissions into the Earth's atmosphere. As a result, BVOCs are heavily involved in key atmospheric processes and play a central role in determining atmospheric composition and the oxidizing capacity of the atmosphere. BVOCs are also believed to make a significant contribution to the organic fraction of atmospheric aerosols. One important group of BVOCs is the C6 oxygenates consisting of species such as (Z)-3-hexenyl acetate, (Z)-3-hexenol and (Z)-3-hexenyl, which are emitted to the atmosphere from vegetation as a result of leaf wounding and have been detected in numerous field studies. In order to determine the potential impact of these biogenic emissions on air quality and tropospheric chemistry in general, we report here the rate coefficients for the ozonolysis of (Z)-3-hexenyl acetate, (Z)-3-hexenol, (Z)-3-hexenyl and the structurally related compound (Z)-3-hexene and reaction products from these reactions. From these results, the effect of a functional group change on the rate coefficient and the contribution from each Criegee intermediate to the OH radical yield may be determined.

Experimental

Experiments on the O3 initiated oxidation of the unsaturated C6 oxygenated hydrocarbons were performed in a 3.9 m3 indoor simulation chamber in our laboratory in Cork. The chamber is equipped with in-situ FTIR for quantifying reactant loss and product formation.

The yields of OH radicals were determined by measuring the loss of a tracer compound, 1,3,5-trimethylbenzene. Propanal yields were measured in the presence of excess carbon monoxide to scavenge the OH radicals formed in the reactions.

Rate Coefficients

Absolute rate measurements for the reaction of ozone with (Z)-3-hexene, (Z)-3-hexenol and (Z)-3-hexenyl acetate were performed under pseudo-first-order conditions: d[OH]/dt = k’[VOC], where k’ is the pseudo-first-order rate coefficient, given by k’ = k[O3]

Reaction Mechanism & Branching Ratios

The branching ratios of each ozone were calculated from the observed propanal yields obtained. The ozone formed from the addition of O3 to (Z)-3-hexenyl acetate significantly favours the formation of propanal, whereas the branching ratios for (Z)-3-hexene are equal and slightly favour the formation of hydroxyl propanal in the case of (Z)-3-hexenol. The significant difference in the case of (Z)-3-hexenyl acetate is likely to be caused from the presence of the acetate functional group.

OH Radical & Propanal Yields

Results obtained are in good agreement with previous work in this area, with the exception of the OH radical yield for (Z)-3-hexenyl acetate which is more than 3 times larger than the value reported in the literature. The reason for such a large discrepancy is not known.

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