Effect of Functional Group on the Reactivity 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 90% 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 C_6 oxygenates consisting of species such as *(Z)*-3-hexenyl acetate, *(Z)*-3-hexenol and *(Z)*-3-hexenal, 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-hexenal 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.
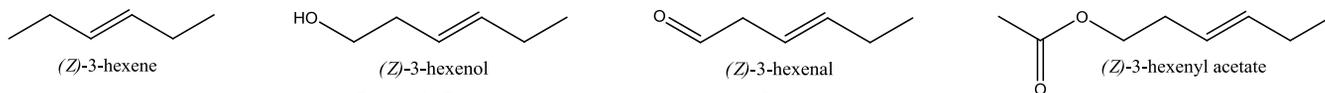

Figure 1. Chemical structures of the unsaturated C_6 oxygenated hydrocarbons

Experimental

Experiments on the O_3 initiated oxidation of the oxygenated hexene derivatives were performed in a 3.9 m^3 indoor simulation chamber in our laboratory in Cork. The chamber is equipped with in-situ FTIR spectroscopy for quantifying reactant loss and product formation.

Figure 2. Atmospheric Simulation Chamber

Absolute rate coefficients were determined under *pseudo*-first-order conditions by monitoring the loss of ozone, using a UV photometric ozone analyser (Thermo 49i) in the presence of a known amount of excess hydrocarbon. The relative rate method was used to determine the rate coefficient for the reaction of ozone with *(Z)*-3-hexenal. The yields of OH radicals were determined by measuring the loss of a tracer compound, 1,3,5-trimethylbenzene (TMB). Propanal yields were measured in the presence of excess carbon monoxide to scavenge the OH radical formed in the reactions.

Rate Coefficients

Under *pseudo*-first order conditions: $-d\ln[O_3]/dt = k'[VOC]$, where k' is the *pseudo*-first-order rate coefficient, given by $k' = k[O_3]$

Figure 3. A first-order plot for the ozonolysis of *(Z)*-3-hexene.

Figure 4. Second-order plots: *(Z)*-3-hexene (red), *(Z)*-3-hexenol (blue) and *(Z)*-3-hexenyl acetate (green).
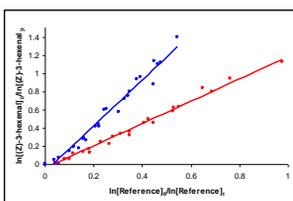
Figure 5. Relative rate plot for the reaction of ozone with *(Z)*-3-hexenal using isoprene (blue) and 2,3-dimethyl-1,3-butadiene (red) as reference compounds.

The order of reactivity, alkene>alcohol>acetate>aldehyde may be explained by the electron-withdrawing strength of the functional groups, which affects electrophilic addition of ozone. The same pattern is observed for the *(E)*-2 isomers, however, in this case, the functional groups are closer to the >C=C< bond and the oxygenated derivatives are therefore less reactive than their *(Z)*-3 counterparts.

VOC	kO_3	kO_3 - Literature
(Z)-3-hexene	11.0 ± 0.82	14.4 ± 0.16
(Z)-3-hexenol	6.52 ± 0.61	6.39 ± 1.66
(Z)-3-hexenyl acetate	4.24 ± 0.14	5.91 ± 0.88
(Z)-3-hexenal	3.19 ± 0.08	Not studied

Table 1. Rate coefficients (10^{-17} cm^3 $molecule^{-1}$ s^{-1}) for *(Z)*-3-hexene and its oxygenated derivatives.

OH Radical and Propanal Yields
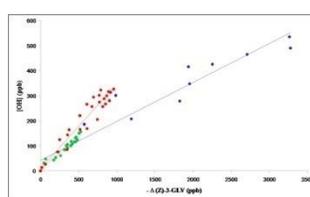

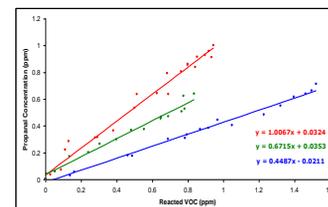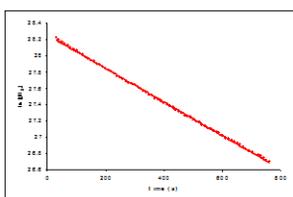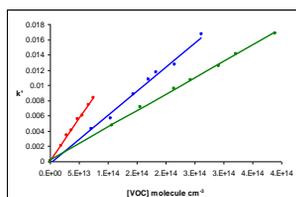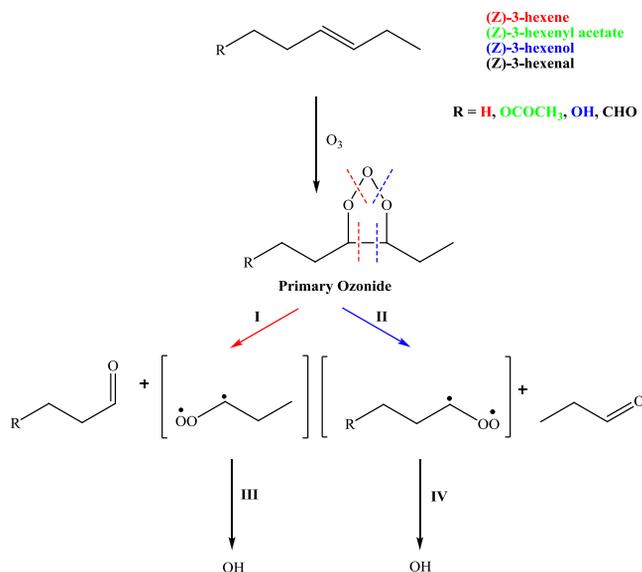**Figure 6.** OH Yield plots: *(Z)*-3-hexene (red), *(Z)*-3-hexenol (blue) and *(Z)*-3-hexenyl acetate (green).

Figure 7. Propanal yield plots: *(Z)*-3-hexene (red), *(Z)*-3-hexenol (blue) and *(Z)*-3-hexenyl acetate (green).

y = 1.0067x + 0.0324
y = 0.6715x + 0.0353
y = 0.4487x - 0.0211

Figure 8. Reaction mechanism.

(Z)-3-hexene
(Z)-3-hexenyl acetate
(Z)-3-hexenol
(Z)-3-hexenal

R = H, OCOCH$_3$, OH, CHO

Primary Ozonide

The propanal yields are higher for the compounds with electron-withdrawing functional groups (aldehyde and acetate) indicating that the formation of these functionalised Criegee Intermediates are preferred over CH_3CH_2CHOO.

The OH yields also show interesting variations, with the functionalised Criegee Intermediate produced from *(Z)*-3-hexenal producing the highest amount of OH.

GLV	I	II	III	IV
(Z)-3-hexenyl acetate	0.33	0.67	0.056	0.094
(Z)-3-hexenol	0.55	0.45	0.094	0.166
(Z)-3-hexenal	0.16	0.84	0.027	0.303
(Z)-3-hexene	0.50	0.50	0.170	0.170

Table 2. Summary of OH radical yields, propanal yields and the contribution of each Criegee intermediate towards the OH radical yield.