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

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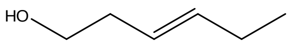
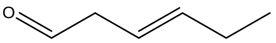
Introduction

Large quantities of volatile organic compounds are emitted directly into the atmosphere from biogenic and anthropogenic sources [1]. 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 [2]. 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.

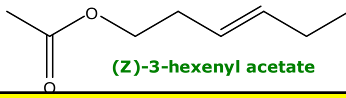
(Z)-3-hexene



(Z)-3-hexenol



(Z)-3-hexenal



(Z)-3-hexenyl acetate

Experimental

Experiments on the O_3 initiated oxidation of the unsaturated C_6 oxygenated hydrocarbons were performed in a 3.9m^3 indoor simulation chamber in our laboratory in Cork. The chamber is equipped with in-situ FTIR for quantifying reactant loss and product formation [3].

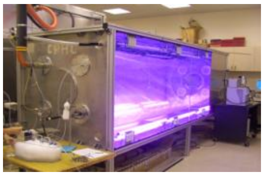


Figure 1. Atmospheric Simulation Chamber

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 [4]. 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 [5]. 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 & (Z)-3-hexenyl acetate with performed under *pseudo*-first-order conditions: -dln[O3]/dt = k' [VOC], where k' is the *pseudo*-first-order rate coefficient, given by k' = k[O3]

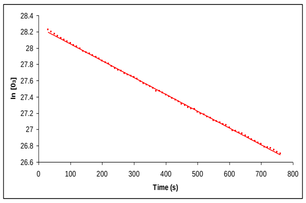


Figure 2. A typical pseudo-first order plot.

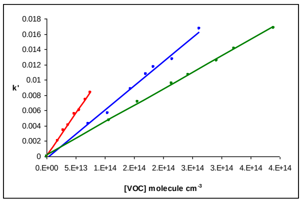


Figure 3. A summary of the second-order plots.

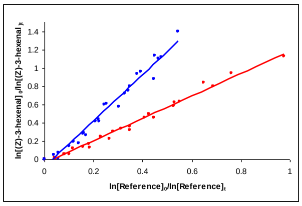


Figure 4. Relative rate plot for the reaction of (Z)-3-hexenal using isoprene (blue) and 2,3-dimethyl-1,3-butadiene (red) as reference compounds.

VOC	kO_3 ($1x10^{-17}$) (molecule/cm^3 s)	kO_3 - Literature ($1x10^{-17}$) (molecule/cm^3 s)
(Z)-3-hexene	11.0 ± 0.82	14.4 ± 0.16 [9]
(Z)-3-hexenol	6.52 ± 0.61	6.39 ± 1.66 [8]
(Z)-3-hexenyl acetate	4.24 ± 0.14	5.91 ± 0.88 [8]
(Z)-3-hexenal	3.18 ± 0.08	No previous study

The rate coefficients for (Z)-3-hexene, (Z)-3-hexenyl acetate and (Z)-3-hexenol are in reasonably good agreement with those previously reported in the literature. The results indicate that the functional group has a noticeable effect on reactivity; the greater the strength of the electron withdrawing group on the hexene derivative, the slower the reaction is with ozone.

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.

VOC	OH Radical Yield	Literature OH Radical Yield	Propanal Yield	Literature Propanal Yield
(Z)-3-hexene	0.34 (± 0.04)	0.36 (± 0.07) [10]	1.00 (± 0.06)	No previous study
(Z)-3-hexenol	0.26 (± 0.02)	0.26 (± 0.09) [8]	0.45 (± 0.02)	0.49 (± 0.07) [6]
(Z)-3-hexenyl acetate	0.55 (± 0.03)	0.16 (± 0.08) [8]	0.67 (± 0.06)	0.76 (± 0.04) [7]

Reaction Mechanism & Branching Ratios

The branching ratios of each ozonide were calculated from the observed propanal yields obtained. The ozonide formed from the addition of O_3 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.

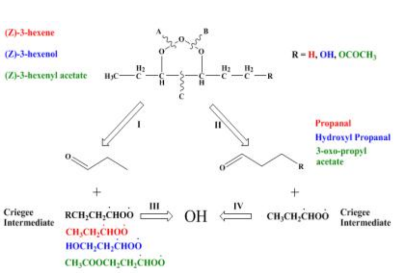


Figure 5. Reaction mechanism

VOC	I	II	III	IV
(Z)-3-hexene	0.50	0.50	0.34	0.34
(Z)-3-hexenol	0.45	0.55	0.16	0.34
(Z)-3-hexenyl acetate	0.67	0.33	0.66	0.34

The contribution of each Criegee intermediate towards the OH radical yield for the series of unsaturated C_6 oxygenated hydrocarbons was calculated based on the assumption that the 0.34 OH radical yield from the CH_3CH_2CHOO biradical for (Z)-3-hexene also contributes the same OH radical yield from this biradical which is also formed in the case of (Z)-3-hexenyl acetate and (Z)-3-hexenol ozonolysis reactions. The structure of the substituted Criegee intermediates clearly has an influence on the OH yield.

References

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