

# STUDIES ON THE ATMOSPHERIC DEGRADATION OF UNSATURATED ACIDS, ESTERS, KETONES AND ALCOHOLS

H. Sidebottom\*(1), R. Morris(1), L. Viero(1), A. Mellouki (2), G. Le Bras(2), T. Vera (3), A. Muñoz (3)

1. University College Dublin, Ireland

2. CNRS-ICARE, Orleans, France

3. Fundacion CEAM, Valencia, Spain

Corresponding author: [howard.sidebottom@ucd.ie](mailto:howard.sidebottom@ucd.ie)

Field measurements indicate that oxygenated volatile organic compounds form a major component of the trace gases found in the troposphere. They are emitted directly into the atmosphere from biogenic sources and from solvent and fuel additives use, and are also formed in the tropospheric oxidation of all hydrocarbons. It is now accepted that a change from aromatic and halocarbon solvents to oxygenated compounds is inevitable both in terms of toxicity problems, and in the case of aromatic compounds as a means of reducing the levels of oxidant formation in the troposphere. It is apparent that oxygenated compounds will thus play an increasing role in determining the oxidising capacity of the troposphere both on a regional and a global scale. This work is concerned with the oxidation of unsaturated acids, esters, ketones and alcohols under atmospheric conditions.

Absolute and relative rate experiments were carried out on the reactions of ozone and hydroxyl radicals with a series of unsaturated oxygenated compounds. Absolute rate coefficients for the reactions were obtained by monitoring the decay of either O<sub>3</sub> or OH radicals under conditions in which the substrate was in excess. Ozone loss was determined using a chemiluminescence technique while OH radical decays were followed using laser induced fluorescence. Rate coefficient data for the reactions were also obtained by monitoring the loss of the substrate relative to the loss of a reference compound whose rate coefficient was reliably known. The decays of the substrate and reference were followed using FTIR spectroscopy and capillary gas chromatography. The rate coefficients were employed to determine structure-activity relationships for the reactions and also the atmospheric lifetimes of the unsaturated oxygenated compounds.

Product distribution studies for the reactions of ozone and hydroxyl radicals with the unsaturated oxygenates were performed at Valencia, Spain (EUPHORE) Reactants and products were monitored by long-path FTIR spectroscopy and gas chromatography. Product identities were confirmed by mass spectrometry. It was evident from the products detected from the reactions of O<sub>3</sub> and OH radicals that the major reaction of both O<sub>3</sub> and OH radicals with the unsaturated oxygenates was electrophilic addition to the double bond system to produce an ozonide or a hydroxy alkyl radical respectively. Further reactions of these intermediates gave the eventual oxidation products of the reactions. The major products of both the reactions of O<sub>3</sub> and hydroxyl radicals with the unsaturated oxygenates were very similar. Reactions with unsaturated acids gave formaldehyde and acid carbonyls, and reactions with the corresponding esters produced ester carbonyls. Acid anhydrides and formaldehyde were found to be the dominant products of the reactions of O<sub>3</sub> and OH radicals with esters of general structure CH<sub>2</sub>=CHO(CO)R. Oxidation of unsaturated ketones led to the formation of dicarbonyl species, while the oxidation of unsaturated alcohols produced hydroxy carbonyl compounds. All the available product yield data suggested that the reactions of both ozone and hydroxyl radicals with unsaturated oxygenates gave rise to the formation of highly oxygenated compounds which are likely to be quite soluble and hence may be susceptible to rainout, or since they have relatively low vapour pressures could be important in aerosol formation.