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Development and validation of the tropospheric degradation mechanisms of ethylene glycol mono-vinyl and di-vinyl ethers

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Vinyl ethers are used increasingly in manufacturing, as solvents and are also being considered as petrol additives. These volatile compounds on emission to the atmosphere can undergo complex chemical reactions which lead to the formation of species which are environmentally damaging, in particular the formation of photochemical oxidants.

As part of the European framework five project MOST (Multiphase chemistry of Oxygenated Species in the Troposphere) detailed atmospheric degradation schemes for the vinyl ether compounds ethylene glycol mono-vinyl ether (MVE-1, CH_2=$CHOCH_2CH_2OH$) and ethylene glycol di-vinyl ether (DVE-1, CH_2=$CHOCH_2CH_2CHO$=CH_2) have been constructed. Each mechanism has been built according to a set of rules as defined by the latest Master Chemical Mechanism (MCM) protocol (Saunders et al., *Atmos. Chem. Phys.*, **3**, 161-180, 2003). Rate constants and product branching ratios are taken from specific experiments performed by members of the MOST consortium or are estimated from structure activity relationships or by analogy. The complete degradation schemes contain 307 and 606 reactions for MVE-1 and DVE-1 respectively.

An intensive photosmog measurement campaign was carried out at the EUPHORE chamber in Valencia between the 5^{th} and 15^{th} April 2005. The aim of the campaign was to deliver a comprehensive suite of data specifically designed to validate the de-

tailed MVE-1 and DVE-1 mechanisms under a variety of atmospheric conditions. The 200 m^3 EUPHORE chamber is highly instrumented, allowing for the accurate analysis of reactants, products and intermediates, including the radical intermediates OH and HO_2. Measurements of HO_x provide crucial information on the radical yields and on the oxidative capacity of the system being studied.

Both the MVE-1 and DVE-1 degradation schemes were incorporated into chamber optimised box models. Ozone Isopleth plots were used to choose the initial conditions for each experiment so that the mechanisms can be evaluated under both NO_x and VOC limited conditions. In the model-measurement inter-comparisons radical budgets have been calculated in order to identify the key reaction pathways of the mechanism.

In general, for both MVE-1 and DVE-1, an early spike in radical production is seen in the model results which can be suppressed to varying degrees by a 5-15 % increase in the nitrate yield of the primary β-hydroxy RO_2 which leads to a generally better prediction of the measurement profiles in both magnitude and shape, except for formaldehyde. However, all models still over predict HO_2 from between factors of 2-5.