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Tropospheric chemical degradation of methyl acrylate and butyl methacrylate initiated by chlorine atoms

M. B. Blanco (1), I. Bejan (2), I. Barnes (2), P. Wiesen (2) and M. Teruel (1)

(1) Instituto de Investigaciones en Fisicoquímica de Córdoba (I.N.F.I.Q.C.), Dpto. de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba. Ciudad Universitaria, 5000 Córdoba, Argentina. (mteruel@fcq.unc.edu.ar);

(2) Physikalische Chemie/FBC, Bergische Universität Wuppertal, Wuppertal, Germany. (barnes@uni-wuppertal.de; ibejan@uni-wuppertal.de)

Unsaturated esters are widely used in industrial processes for the production of polymers, paper coating, paint formulations, etc. The sources of their emissions include among others the manufacture of plastics, aircraft and electronic components. While the OH radical is considered to be the major daytime oxidant for the marine environment and coastal areas, reaction with Cl atoms has been shown to be an additional and sometimes potentially significant removal process of these compounds. In the present study we report for the first time, the determination of rate constants for the reactions of Cl atoms with methyl acrylate (k_1) and butyl methacrylate (k_2), using a relative kinetic method.

The rate constants were measured relative to both isobutene and 1,3-butadiene as reference compounds in 1 atm of air at 298 K. All the experiments were performed in a 1080 l quartz-glass photoreactor using *in situ* FTIR analysis to monitor the decay of the organics. The following rate constants (cm^3 molecule^{-1} s^{-1}) were obtained:

k_1= (2.14±0.54) × 10^{-10} and k_2 =(3.77±0.82) × 10^{-10}

The kinetic data will be presented together with an assessment of the atmospheric importance of the chlorine initiated degradation. In addition, results from product studies of the Cl atom initiated oxidation of the unsaturated esters will be presented. Based on the available information a possible degradation mechanism for Cl reaction of the

compounds has been elucidated and will also be discussed.