



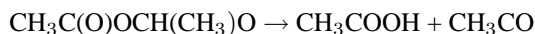
## Atmospheric chemistry of esters

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Esters are naturally occurring molecules, responsible for the tastes and aromas of many fruits. However, a larger atmospheric source is thought to be the oxidation of oxygenated organics such as ethers. The increased use of oxygenated fuels is expected to lead to enhanced concentrations of esters such as methyl formate and t-butyl formate in the atmosphere.

The atmospheric oxidation pathways of esters are not fully elucidated. A few years ago Tuazon et al. (*J. Phys. Chem. A* 102, 1998, 2316) identified a novel pathway, the 5-membered  $\alpha$ -ester elimination mechanism, for  $\alpha$ -oxy radicals formed in the oxidation of ethyl acetate.



Since then a number of papers have appeared concerning the oxidation of acetates (Christensen et al., *J. Phys. Chem. A* 104, 2000, 345; Picquet-Varrault et al., *PCCP* 3, 2001, 2595; *J. Phys. Chem. A* 106, 2002, 2895). However, less attention has been directed toward formates (Good et al., *J. Phys. Chem. A* 104, 2000, 1505; Wallington et al., *J. Phys. Chem. A* 105, 2001, 5146). We have studied the oxidation of methyl acetate, methyl formate, isopropyl formate and t-butyl formate, using both Cl atoms and OH radicals to initiate the reaction. Results will be presented on the site of attack and on the subsequent oxidation pathways. Attack at the formyl group H-C(O) is substantial in all the systems studied, contrary to simple structure-activity rules. In addition to the alpha-ester reaction, decomposition and isomerisation pathways are also shown to occur. Overall oxidation mechanisms for these species will be presented,

and the behavior of these highly oxygenated species will be contrasted with that of simple hydrocarbons in terms of the energetics of the radicals involved.