

Kinetic studies of the reactions of Cl atoms with Esters by a technique of pulsed laser photolysis VUV-LIF spectroscopy

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Esters are an important class of oxygenated volatile organic compounds used in food flavorings and in perfumes. They are present in fruits and are emitted to the atmosphere naturally. Esters are formed in the atmosphere as a product of the oxidation of ethers. Accurate kinetic data for reactions of Cl atoms with esters are needed in atmospheric chemistry for two reasons. First, they are introduced into global atmospheric models to assess the loss of organics via reaction with Cl atoms in the marine boundary layer. Second, they are used to analyze data from smog chamber experiments in which chlorine atoms are used to initiate the oxidation of organic compounds.

In this work a technique of pulsed laser photolysis vacuum ultraviolet laser-induced fluorescence spectroscopy were used to study the reactivity of Cl($^2P_{3/2}$) atoms with a series of formates in ~ 6 Torr of Ar at 295 ± 2 K. Rate constants were determined for the following compounds: methyl formate, $(2.75 \pm 0.12) \times 10^{-12}$; ethyl formate, $(1.15 \pm 0.48) \times 10^{-11}$; *n*-propyl formate, $(5.16 \pm 0.11) \times 10^{-11}$; *n*-butyl formate, $(1.51 \pm 0.53) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹.

In recent work we noted a systematic discrepancy of approximately 20-30% between results from relative and absolute rate studies of the kinetics of reactions of Cl atoms with a series of formates include methyl formate, ethyl formate, *n*-propyl formate and *n*-butyl formate.

One of our results for methyl formate is approximately a factor of 1.5 greater than reported from recent absolute rate study and approximately a factor of 2 greater than reported from recent relative rate studies. Our result for ethyl formate is more conformable to relative rate studies than absolute rate study. Our result for *n*-propyl formate is intermediate between absolute rate study and relative rate studies. And our result for *n*-butyl formate is more conformable to absolute rate study than relative rate studies. The likely origin of these discrepancies are discussed.