

Hydroxyl Radical Reactions with Halogenated Ethanols in Aqueous Solution

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A laser-photolysis long-path absorption (LP-LPA) set-up was used to investigate OH radical reactions with halogenated alcohols in the aqueous phase. Partially halogenated alcohols have been suggested as alternative to CFCs and HCFCs, therefore their atmospheric concentrations are expected to increase in the near future. Due to their polarity, uptake by cloud water and rain might be a significant sink for these chemicals in the atmosphere. In the aqueous phase, fluorinated and chlorinated alcohols are suggested to react mainly with OH radical. However only few kinetic data are available in the literature, thus the reactions of OH radical with the following organic compounds have been studied: (1) 2-fluoroethanol, (2) 2,2-difluoroethanol, (3) 2,2,2-trifluoroethanol, (4) 2-chloroethanol, (5) 2,2-dichloroethanol, and (6) 2,2,2-trichloroethanol.

The kinetics studies have been carried out by competition kinetics techniques using the thiocyanate anion as a reference reactant at temperature between 288 and 328 K and the following kinetic data have been obtained: (1) 2-fluoroethanol, ($k_1(298\text{ K}) = (7.4 \pm 0.6) \cdot 10^8\text{ M}^{-1}\text{ s}^{-1}$; $A_1 = (1.2 \pm 0.1) \cdot 10^{12}\text{ M}^{-1}\text{ s}^{-1}$; $E_{A1} = (16.9 \pm 10.7)\text{ kJ mol}^{-1}$); (2) 2,2-difluoroethanol, ($k_2(298\text{ K}) = (2.55 \pm 0.2) \cdot 10^8\text{ M}^{-1}\text{ s}^{-1}$; $A_2 = (4.5 \pm 0.5) \cdot 10^9\text{ M}^{-1}\text{ s}^{-1}$; $E_{A2} = (7.1 \pm 6.6)\text{ kJ mol}^{-1}$); (3) 2,2,2-trifluoroethanol, ($k_3(298\text{ K}) = (0.63 \pm 0.20) \cdot 10^8\text{ M}^{-1}\text{ s}^{-1}$; $A_3 = (2.0 \pm 0.1) \cdot 10^{11}\text{ M}^{-1}\text{ s}^{-1}$; $E_{A3} = (20 \pm 7)\text{ kJ mol}^{-1}$); (4) 2-chloroethanol, ($k_4(298\text{ K}) = (8.3 \pm 0.8) \cdot 10^8\text{ M}^{-1}\text{ s}^{-1}$; $A_4 = (3.0 \pm 0.2) \cdot 10^{10}\text{ M}^{-1}\text{ s}^{-1}$; $E_{A4} = (9 \pm 4)\text{ kJ mol}^{-1}$); (5) 2,2-dichloroethanol, $k_5(298\text{ K}) = (4.0 \pm 0.4) \cdot 10^8\text{ M}^{-1}\text{ s}^{-1}$; $A_5 = (2.1 \pm 0.2) \cdot 10^{10}\text{ M}^{-1}\text{ s}^{-1}$; $E_{A5} = (10 \pm 4)\text{ kJ mol}^{-1}$); (6) 2,2,2-trichloroethanol, $k_6(298\text{ K}) = (2.5 \pm 0.2) \cdot 10^8\text{ M}^{-1}\text{ s}^{-1}$; $A_6 = (1.6 \pm 0.1) \cdot 10^{10}\text{ M}^{-1}\text{ s}^{-1}$; $E_{A6} = (10 \pm 5)\text{ kJ mol}^{-1}$. The stated errors are statistical errors for a confidence interval of 95%.

The kinetic data obtained here will be used as input parameters in forthcoming versions of the multiphase reaction mechanism CAPRAM.