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Direct Rate Constants for the Reaction of OH Radicals with Fluoro-Alcohols and Acetyl-Fluoride

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As a result of the Montreal Protocol (1987), the fluoro-alcohols have gained an increasing importance proposed as replacement industrial materials for freons. Fluoro-alcohols have zero ozone depletion potential, but they still must be considered as possible greenhouse gases contributing to global warming due to the strong IR activity of the C–F bonds. These compounds degrade in the atmosphere via a series of reactions initiated by OH radicals, thus their atmospheric lifetime is essentially determined by the reaction rate coefficients with OH.

The kinetics of the reactions of OH radicals with 2,2-difluoro-ethanol (1) and 2,2,2-trifluoro-ethanol (2) have been studied by using the laser flash photolysis-resonance fluorescence experimental technique. OH radicals were produced by the 248 nm exciplex laser photolysis of HNO_3. The following reaction rate coefficients were determined: k_1 (300 K) = (2.52 $\pm$ 0.44) 10^{-13} and k_2 (300 K) = (1.06 $\pm$ 0.30) 10^{-13} cm^3 $molecule^{-1}$ s^{-1} with 2σ precision given. k_1 is the first direct kinetic data for the reaction of OH radicals with CF_2HCH_2OH reported in the literature.

Acetyl-fluoride is the primary atmospheric degradation product of HFC-152a which is a widely used freon substitute. Reaction of OH radicals with $CH_3C(O)F$ (3) has been studied experimentally using the discharge flow technique combined with resonance fluorescence monitoring of OH radicals. OH radicals were obtained by reacting H atoms with NO_2 generated in microwave discharge. A room temperature bimolecular rate constant of k_3 (298 K) = (7.40 $\pm$ 0.48) 10^{-15} cm^3 $molecule^{-1}$ s^{-1} was obtained for reaction OH + $CH_3C(O)F$ which appears to be the first quantitative kinetic data for this reaction.

Fluorine substitution has been found to reduce the reactivity in the hydrogen abstrac-

tion reactions studied in accordance the known electrophil nature of the OH radical.