RATE CONSTANTS AND DEUTERIUM KINETIC ISOTOPE EFFECTS FOR METHOXY RADICAL REACTING WITH NO_2 AND O_2

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Alkoxy radicals (RO) are important intermediates in the photooxidation of volatile organic compounds due to their great impacts on ozone formation and gas-particle partitioning of stable oxidation products. Methoxy radical (CH_3O) is the prototype for all alkoxy radicals. The absolute rate constants k_{NO2}(T) for reaction of CH_3O and $CD_3O$with NO_2 have been measured using laser flash photolysis to generate radicals and laser-induced fluorescence for time-resolved detection. The pressure and temperature dependence for k_{NO2} have been observed over the range 30-700 Torr and 250-335 K. This will be the first direct measurement of k_{NO2} for CH_3O near ambient pressure and the first ever for CD_3O.The relative rate constants k_{NO2}/k_{O2}(T) have been measured in an environmental chamber with FTIR detection. This combination enables the first determination of k_{O2} (T) for CH_3O and CD_3O for $T < 298$ K. The results will also help validate theoretical methods for studying alkoxy + O_2 reactions, which are challenging for quantum chemistry.