

RATE CONSTANTS AND DEUTERIUM KINETIC ISOTOPE EFFECTS FOR METHOXY RADICAL REACTING WITH NO₂ AND O₂

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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 (CH₃O) is the prototype for all alkoxy radicals. The absolute rate constants $k_{NO_2}(T)$ for reaction of CH₃O and CD₃O with NO₂ 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_{NO_2} have been observed over the range 30-700 Torr and 250-335 K. This will be the first direct measurement of k_{NO_2} for CH₃O near ambient pressure and the first ever for CD₃O. The relative rate constants $k_{NO_2}/k_{O_2}(T)$ have been measured in an environmental chamber with FTIR detection. This combination enables the first determination of $k_{O_2}(T)$ for CH₃O and CD₃O for $T < 298$ K. The results will also help validate theoretical methods for studying alkoxy + O₂ reactions, which are challenging for quantum chemistry.