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Rate constant for the reaction of OH with methyl iodide, a re-determination by flash photolysis of water vapour and time resolved resonance fluorescence of OH

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Methyl iodide is a major source gas for atmospheric iodine, and it is mainly emitted from the ocean. Aqueous-phase reactions, such as hydrolysis and exchange reactions with chloride control its emissions to the atmosphere, where its lifetime is limited to less than a week, mainly by photolysis. A minor contribution to the loss processes in the troposphere is the gas-phase reaction with OH radicals, that has been investigated by several authors. On the other hand, this reaction turned out to be uncertain in spite of interest in nuclear safety after the International Phebus Fission Product programme, initiated in 1988. Some of the most important observed phenomena with regard to the chemistry of iodine were not predicted, clearly showing the need for carrying out rate constant determinations for the reactions of I_2 and CH_3I with OH, which is a major oxidant product from the air radiolysis under accident conditions. We have measured the rate constant for the reaction $OH + CH_3I \rightarrow H_2O + CH_2I$ in He at 260 mbar in the temperature range from 298 to 362 K. OH radicals were produced by flash photolysis of H_2O in the vacuum-UV at wavelengths $>$ 115 nm using a Xe flash lamp with a MgF_2 window. Time profiles of OH radicals are monitored by resonance fluorescence of the $A^2\ \Sigma \rightarrow X^2\ \Pi$ transition at 308 nm, induced by the emission from a microwave discharge of a flow of He and H_2O, a few Torr each. The signal is monitored by photon counting and multichannel scaling, collecting the counts from 50 flashes each, obtaind by pulsed photolysis of various mixtures of H_2O and CH_3I under slow-flow conditions. Decays of OH in the presence of CH_3I are observed to be exponential, and the decay rates are found to be linearly dependent on the concentration of CH_3I. Rate constants, $k \pm 2\sigma$ (in units of 10^{-14} cm^3 s^{-1}) of 4.14±0.20, 6.33±0.68, 7.31±1.18 and 8.24±1.60 at 298, 326, 352 and 362 K, respectively, are obtained from linear regressions and lead to an Arrhenius expression of $k = 1.5\times10^{-12}$ exp (-1067 K / T) cm^3 s^{-1} . These rate constants are significantly below the present IUPAC recommendation. The consequence is an even smaller contribution of the OH reaction to tropospheric degradation.

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