Temperature Dependence of the Rate Constant for the CH_3 Recombination Reaction: A Loss Process in Outer Planet Atmospheres

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The methyl free radical (CH_3) has been observed in the atmospheres of Saturn, Neptune, and recently by Cassini - CIRS in Jupiter. The recombination of methyl radicals is the major loss process for methyl in the atmospheres of Saturn and Neptune. The serious disagreement between observed and calculated levels of CH_3 has led to suggestions that the atmospheric models greatly underestimated the loss of CH_3 due to poor knowledge of the rate of the reaction $CH_3 + CH_3 + M \rightarrow C_2H_6 + M$ at the low temperatures and pressures of these atmospheric systems.

In an attempt to resolve this problem, we undertook in our laboratory the measurement of the absolute rate constant for the self-reaction of CH_3 at T = 155, 202 and 298 K and P = 0.6 - 2.0 Torr nominal pressure (He). The experimental technique is discharge fast flow with mass spectrometric detection and monitoring of the CH_3 decay. The methyl radical is generated via the fast reaction $F + CH_4 \rightarrow CH_3 + HF$. The results were obtained by graphical analysis of plots of the reciprocal of the CH_3 signal versus reaction time. Since this is a second order reaction, absolute initial concentrations of the CH_3 radicals had to be measured by separate calibration experiments.

The experimental results show that the reaction is in the fall-off region at T = 202 and 298 K. At T = 298K, k(0.6 Torr) = 2.15 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} and k(1 Torr) = 2.44 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} At T = 202K, the rate constant increased from k(0.6 Torr) = 5.04 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} to k(1.0 Torr) = 5.25 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} to k(2.0 Torr) = 6.52 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. At T = 155 K, the results indicate that the reaction is either at the high pressure limit or so close that we cannot measure a pressure effect upon the rate constant. At T = 155K, k(0.6 Torr) = 6.82 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, k(1.0 Torr) = 6.98 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} and k(1.5 Torr) = 6.91 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. These experimental results will be compared with those from theoretical calculations.

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