

# Temperature Dependence of the Rate Constant for the CH<sub>3</sub> Recombination Reaction: A Loss Process in Outer Planet Atmospheres

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## 1. Introduction

The methyl free radical (CH<sub>3</sub>) has been observed in the atmospheres of Saturn and Neptune by the ISO satellite. There are discrepancies between the column densities for the CH<sub>3</sub> radical derived from the ISO observations and the column densities derived from atmospheric photochemical models. For Neptune the model column density is 1.5 times that derived from ISO. For Saturn the model is 6 times that from ISO. The recombination of methyl radicals is the major loss process for methyl in these atmospheres. The serious disagreement between observed and calculated levels of CH<sub>3</sub> has led to suggestions that the atmospheric models greatly underestimated the loss of CH<sub>3</sub> due to poor knowledge of the rate of the reaction (1) CH<sub>3</sub> + CH<sub>3</sub> + M → C<sub>2</sub>H<sub>6</sub> + M at the low temperatures and pressures of these atmospheric systems. Although the reaction CH<sub>3</sub> + CH<sub>3</sub> + M → C<sub>2</sub>H<sub>6</sub> + M has been extensively studied both theoretically and experimentally, the laboratory conditions have been, with only a few exceptions, higher temperatures (T ≥ 298K), higher pressures (P ≥ 10 Torr - 13.3 mbar) or M = Ar rather than H<sub>2</sub> or He as the bath gas.

## 2. Experimental

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<sub>3</sub> at T = 155, 202 and 298 K and P = 0.6 - 2.0 Torr nominal pressure with He as the bath gas. The experimental technique is discharge fast flow with mass spectrometric detection and monitoring of the CH<sub>3</sub> decay. The methyl radical is generated via the fast reaction F + CH<sub>4</sub> → CH<sub>3</sub> + HF. A microwave discharge generates the fluorine atoms. The CH<sub>4</sub> reagent is added through the moveable injector, which allows the CH<sub>3</sub> mass spectrometric signals to be measured versus distance and therefore time. Methane was in large excess to ensure rapid and quantitative conversion of F to CH<sub>3</sub>. The absolute concentration of fluorine atoms used to generate CH<sub>3</sub> was determined by measuring the consumption of Cl<sub>2</sub> in the fast titration reaction F + Cl<sub>2</sub> → Cl + FCl. The methyl radicals

were detected at  $m/z = 15$  following low-energy (10 - 11 eV) electron impact ionization. Since large concentrations of methane were required, the low electron energy prevented dissociative ionization of  $\text{CH}_4$  to yield  $\text{CH}_3^+$ . A cooling jacket surrounds the tubular flow tube to vary the temperature of the gas flow. At 202K, the coolant was ethanol circulated from a commercial chiller. At 155K, the coolant was nitrogen gas which had flowed through a copper coil immersed in liquid nitrogen.

Since the recombination reaction of the  $\text{CH}_3$  radicals is second order in  $\text{CH}_3$ , absolute concentrations of the radical are needed for the kinetic data analysis. Integration of the second order rate equation, i.e.,  $-(d[\text{CH}_3])/dt = 2 k_1 [\text{CH}_3]^2$ , yields the analytical expression for data analysis: Equation 1:  $(1/[\text{CH}_3]_t) - (1/[\text{CH}_3]_0) = 2k_1 t$ , where  $[\text{CH}_3]_t$  is the absolute methyl concentration at time =  $t$ ,  $[\text{CH}_3]_0$  is the concentration at time = 0 and  $k_1$  is the rate constant for the methyl recombination reaction. The slope of the plot of the inverse of the mass spectrometric signal versus time yields the rate constant via a scaling factor. The  $[\text{CH}_3]$  equals the measured mass spectrometric signal times a scaling factor (SF). SF can be determined from ratio of the absolute methyl concentration to the corresponding mass spectrometric signal at  $m/z = 15$ . However, the absolute  $[\text{CH}_3]$  comes from the F atom titration and hence gives  $[\text{CH}_3]$  at  $t = 0$ , while the signal is recorded at  $t =$  about 3 ms and beyond due to the limitation of finite time for mixing at the tip of the injector and perturbations in flow near the end of the flow tube. For the case of a first order signal decay this is easily handled by a short, linear extrapolation of the signal back to  $t = 0$  in a plot of  $\ln(\text{signal})$  versus time. In the present experiments which are second order in  $\text{CH}_3$ , plotting the inverse of the signal versus time yielded the expected linear plots according to Equation 1. However, extrapolation to  $t = 0$  did not yield reasonable and consistent values for the signal at  $t = 0$  and hence the scaling factor. Although the signal decay is mostly second order in  $\text{CH}_3$ , there are some first order components. Therefore, the scaling factor had to be determined from a calibration decay measurement at low initial methyl concentration.

For the calibration experiments, the methyl concentration was reduced to the lowest possible level where the signal level could still be quantitatively recorded. This was  $[\text{CH}_3] = (2-4) \times 10^{11}$  molecules  $\text{cm}^{-3}$ . Under these conditions, the signal appeared to exhibit good first order decay, although kinetic modeling showed there is a substantial second order contribution. To verify the correctness of these calibration experiments, a number of them were performed with added molecular chlorine in considerable excess, i.e.  $[\text{Cl}_2] = (2-3) \times 10^{13}$  molecules  $\text{cm}^{-3}$ . Under these conditions, the  $\text{CH}_3$  decays largely by the reaction:  $\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}$ . The methyl decay is strictly first order, and the methyl signal at  $t = 0$  is determined by a short linear extrapolation. Then, the absolute methyl concentration at  $t = 0$  is determined by a titration of the F atoms with  $\text{Cl}_2$  as described above for the rate constant decay measurements. Therefore, each experiment required two decay measurements and two F atom titrations.

### 3. Results

For each temperature and pressure the methyl concentration was varied by at least a factor of two to verify the independence of the rate constant with concentration. The  $[\text{CH}_3]$  ranged

from  $(1.2 \text{ to } 10.8) \times 10^{12}$  molecules  $\text{cm}^{-3}$ . The rate constants ( $k_1$ ) are presented below in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The experimental results show that the reaction is in the fall-off region at  $T = 202$  and  $298$  K. At  $T = 298\text{K}$ ,  $k_1(0.6 \text{ Torr}) = 2.15 \times 10^{-11}$  and  $k_1(1 \text{ Torr}) = 2.44 \times 10^{-11}$ . At  $T = 202\text{K}$ , the rate constant increased from  $k_1(0.6 \text{ Torr}) = 5.04 \times 10^{-11}$  to  $k_1(1.0 \text{ Torr}) = 5.25 \times 10^{-11}$  to  $k_1(2.0 \text{ Torr}) = 6.52 \times 10^{-11}$ . 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  $T = 155\text{K}$ ,  $k_1(0.6 \text{ Torr}) = 6.82 \times 10^{-11}$ ,  $k_1(1.0 \text{ Torr}) = 6.98 \times 10^{-11}$  and  $k_1(1.5 \text{ Torr}) = 6.91 \times 10^{-11}$ .

The rate constants for the methyl self-recombination as measured in this study are appropriate for the atmospheric models of Saturn and Neptune in temperature but not in pressure. The lowest pressure we could reach in the flow system is about 0.6 Torr. Therefore, these results will have to be combined with theory to derive the rate constants needed for the atmospheric physical conditions of the outer planets. The experimental rate constants measured in this study and those measured by Slagle *et al.*(1988) are being used to test the derivation of an analytical expression for the rate constant as a function of both pressure and temperature. The analytical expression will then provide the rate constants at lower pressures for use in the photochemical models of the planetary atmospheres.

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#### REFERENCES

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