Temperature Dependence of the Rate Constant for the CH₃ Recombination Reaction:
A Loss Process in Outer Planet Atmospheres

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1. Introduction

The methyl free radical (CH₃) has been observed in the atmospheres of Saturn and Neptune by the ISO satellite. There are discrepancies between the column densities for the CH₃ 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 CH₃ has led to suggestions that the atmospheric models greatly underestimated the loss of CH₃ due to poor knowledge of the rate of the reaction \( 1 \text{ CH}_3 + \text{CH}_3 + \text{M} \rightarrow \text{C}_2\text{H}_6 + \text{M} \) at the low temperatures and pressures of these atmospheric systems. Although the reaction \( \text{CH}_3 + \text{CH}_3 + \text{M} \rightarrow \text{C}_2\text{H}_6 + \text{M} \) has been extensively studied both theoretically and experimentally, the laboratory conditions have been, with only a few exceptions, higher temperatures \((T \geq 298 \text{K})\), higher pressures \((P \geq 10 \text{ Torr - 13.3 mbar})\) or \(\text{M} = \text{Ar}\) rather than \(\text{H}_2\) 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 CH₃ 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 CH₃ decay. The methyl radical is generated via the fast reaction \( \text{F} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{HF} \). A microwave discharge generates the fluorine atoms. The CH₄ reagent is added through the moveable injector, which allows the CH₃ 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 CH₃. The absolute concentration of fluorine atoms used to generate CH₃ was determined by measuring the consumption of Cl₂ in the fast titration reaction \( \text{F} + \text{Cl}_2 \rightarrow \text{Cl} + \text{FCl} \). 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 CH₄ to yield CH₃⁺. 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 CH₃ radicals is second order in CH₃, absolute concentrations of the radical are needed for the kinetic data analysis. Integration of the second order rate equation, i.e., -(d[CH₃]/dt = 2 k₁ [CH₃]², yields the analytical expression for data analysis: Equation 1: (1/[CH₃]ₜ) - (1/[CH₃]₀) = 2k₁t, where [CH₃]₀ is the absolute methyl concentration at time = t, [CH₃]₀ is the concentration at time = 0 and k₁ 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 [CH₃] 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 [CH₃] comes from the F atom titration and hence gives [CH₃] 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(signal) versus time. In the present experiments which are second order in CH₃, 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 CH₃, 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 [CH₃] = (2-4)x10¹¹ molecules 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. [Cl₂] = (2-3)x10¹³ molecules cm⁻³. Under these conditions, the CH₃ decays largely by the reaction: CH₃ + Cl₂ → CH₂Cl + 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 Cl₂ 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 [CH₃] ranged
from (1.2 to 10.8) \times 10^{12} \text{ molecules cm}^{-3}. The rate constants \((k_1)\) are presented below in units of cm\(^3\) molecule\(^{-1}\) 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 \(k_1(1 \text{ Torr}) = 5.25 \times 10^{-11}\) to \(k_1(2.0 \text{ Torr}) = 6.52 \times 10^{-11}\). At \(T = 155\text{ K}\), 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