Low-Temperature Hydrocarbon Photochemistry: $CH_3 + CH_3$ Recombination in Giant Planet Atmospheres

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Planetary emissions of the methyl radical CH_3 were observed for the first time in 1998 on Saturn and Neptune by the ISO (Infrared Space Observatory) mission satellite. CH_3 is produced by VUV photolysis of CH_4 and is the key photochemical intermediate leading complex organic molecules on the giant planets and moons. The CH_3 emissions from Saturn were unexpectedly weak. A suggested remedy is to increase the rate of the recombination reaction

$$CH_3 + CH_3 + H_2 \rightarrow C_2H_6 + H_2$$

at 140 K to a value at least 10 times that measured at room temperature in rare gases, but within the range of disagreeing theoretical expressions at low temperature.

We are performing laboratory experiments at low temperature and very low pressure. The experiments are supported by RRKM theoretical modeling that is calibrated using the extensive combustion literature. The distinction between "high" and "low" pressure is a significant one. In the so called "low pressure limit" the rate of recombination is limited by the rate of stabilization or energy removal by the third body called "M" (really H_2), and the overall recombination rate coefficient is written as

$$k_{recomb}(M \rightarrow 0) \sim k_0[M]$$

In the "high pressure limit" the buffer gas pressure is sufficiently high to stabilize every collision complex, and the overall recombination rate coefficient becomes pressure independent:

$$k_{recomb}(M \rightarrow \infty) \sim k_\infty$$

RRKM calculations indicate that k_0 rises with decreasing temperature much faster than does k_∞. We used 3 different transition state approaches to calculate temperature dependent values for k_∞, and 3 ways to determine the pressure dependence and k_0, including master equation computations. This effort is designed to provide a good predictive fit to the existing experimental rate data [1,2], and thus furnish a reliable theoretical extrapolation to the lower planetary temperatures and pressures. Previous theory has neglected these conditions. Our recommendations for 65-300K in a hydrogen atmosphere are:

$$k_\infty = 3.59\times10^{-10}\ T^{-.262}\ e^{-37/T}\ cm^3\ mol^{-1}\ s^{-1}$$

$$k_0 = 3.32\times10^{-15}\ T^{-2.28}\ e^{131/T}\ cm^6\ mol^{-2}\ s^{-1}$$

Recommended values for helium and argon bath gases are 50% and 70%, and the falloff is described by a Troe factor F = 0.56 [3].

These results mean that low temperature laboratory experiments need to be performed at quite low pressures, say 0.01 mbar or less in order to extrapolate more reliably to the 0.001 mbar and below characteristic of the relevant regions of the giant planet atmospheres. This is consistent with the recent work in Stief's laboratory [2], in which no pressure dependence was observed at 155 and 202 K for pressures from 0.6 to 2.6 mbar. Our present expression does slightly overpredict their lowest pressure results at 298 K.

We are currently measuring the methyl recombination rate constants using a low pressure Knudsen cell photolysis reactor. The technique photolyzes methyl iodide with quadrupled Nd:YAG laser radiation at 255 nm. Precursor loss and ethane product yields are measured by mass spectrometer at the cell exit aperture. Typical pressure ranges are 0.01 - 0.05 mbar. This method was previously used to measure CF_3 recombination rates [4].

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