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:

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

Calculations will be presented that indicate that k_0 rises with decreasing temperature much faster than does k_∞. 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 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 [1,2], in which no pressure dependence was observed at 155 and 202 K for pressures from 0.6 to 2.6 mbar.

References:

[1] R. J. Cody, *et al.*, "Rate Constant for the Recombination of CH_3 Free Radicals: A Loss Process in Outer Planet Atmospheres," *Bull. AAS* **32**, 1020 (2000).
[2] R. J. Cody, *et al.*, "Rate Constant for the CH_3 Recombination Reaction at 155 K: A Loss Process in Outer Planet Atmospheres," *Bull. AAS* **33**, 1080 (2001).

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