

# Kinetics of the CH<sub>3</sub> + Cl Recombination Reaction at High Pressures

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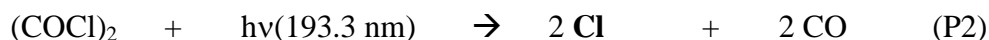
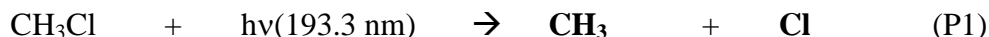
Chlorine atom (Cl) is an important species in the atmosphere. In the remote stratosphere, the major pathway of Cl atoms removal is through the reaction with methane CH<sub>4</sub>:



Methyl radicals formed in reaction 1 might provide an additional pathway to consume chlorine atoms via reaction 2.

In the most recent direct experimental and computational study of reaction 2, Parker et al.<sup>1</sup> employed the discharge flow-mass spectrometry technique. The rate constant was measured over the temperature range of 202–298 K at 0.3–2.0 Torr in helium as buffer gas. The reported pressure dependent rate constants are smaller than  $1.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over this pressure range. The high-pressure limit rate constant based on the RRKM calculations is  $6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

In this work, reaction 2 was studied at near the high pressure limit conditions. Methyl radicals and chlorine atoms were produced directly in photolysis of methylchloride CH<sub>3</sub>Cl at 193.3 nm (ArF excimer laser). Oxalyl chloride (COCl)<sub>2</sub>, a clean photolysis source of Cl atoms, was used to supply additional Cl atoms:



The measurements were performed at ambient temperature over the 30–100 bar pressure range. The decays of CH<sub>3</sub> were monitored via absorption at 216.4 nm with the Cl atoms concentrations in excess of 5–10 times over the CH<sub>3</sub> concentrations.

The preliminary results at two pressures (30 and 100 bar, 298 K, He) are:

$$k_2 = (2.9 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (30 \text{ bar, } 298 \text{ K})$$

$$k_2 = (2.3 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (100 \text{ bar, } 298 \text{ K})$$

Extension of the study to higher temperatures (up to 834 K) as well as wider pressure range (0.01–100 bar) is planned.

(1) Parker, J. K.; Payne, W. A.; Cody, R. J.; Nesbitt, F. L.; Stief, L. J.; Klippenstein, S. J.; Harding, L. B., *J. Phys. Chem. A* **2007**, *111* (6), 1015–1023.