

Kinetics of the $\text{Cl}(^2\text{P}_J) + \text{CH}_4$ Reaction: Effects of Secondary Chemistry Below 300 K

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Abstract

atmospheric chemistry

Absolute rate data for the $\text{Cl}(^2\text{P}_J) + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$ reaction have been obtained from 218 to 298 K by using the discharge-flow resonance fluorescence technique at 1 Torr total pressure. The result at 298 K is $(10.1 \pm 0.6) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The temperature dependence in Arrhenius form is $(6.5 \pm 0.9) \times 10^{-12} \exp[(-1235 \pm 34) / T]$. The errors given are one standard deviation; overall experimental error is estimated at $\pm 15\%$. Because of the relatively large disagreement among earlier measurements at low temperatures, the results were examined for possible effects of non-Boltzmann spin distribution and vibrational excitation of CH_4 , secondary chemistry of CH_3 radicals, and impurities in the CH_4 source. There was no significant change in the observed rate constant when an efficient spin quencher, CF_4 , was added and estimates indicate that vibrational partitioning in CH_4 should be at the ambient reactor temperature before the start of the reaction. The results were also independent of the source of Cl atoms (microwave discharge or thermal decomposition of Cl_2) and whether CH_4 was purified *in-situ*. However, the observed rate constant did depend on initial Cl atom concentrations and to a lesser extent on CH_4 concentrations. Numerical simulations were used to assess the importance of secondary chemistry over a range of reactant concentrations