

The Reaction of Methylidyne with Methane: Role of the Quartet Electronic State

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The reaction of methylidyne (CH) with methane, which plays an important role in combustion and planetary atmospheres, is characterized with high accuracy coupled-cluster calculations. The reaction on the quartet state potential energy surface (PES) is predicted to lead to direct H-abstraction with a small barrier of $2.2 \text{ kcal mol}^{-1}$, yielding triplet CH_2 and CH_3 . The reaction on the doublet state PES is barrierless, involving an insertion/elimination mechanism that leads to the hot intermediate C_2H_5 , which promptly dissociates to $\text{H} + \text{C}_2\text{H}_4$. The results obtained from a statistical chemical kinetics analysis show that the quartet channel makes a negligible contribution to the overall kinetics below 500 K, but becomes competitive with the doublet pathway at the higher temperatures characteristic of hydrocarbon flames. Reaction rate coefficients calculated from first principles are in excellent agreement (within 20%) with experimental values where they are available (200–800 K). For the higher temperatures of combustion environments (where experimental data are lacking), the present study provides reliable high-level results suitable for kinetics modeling.