

Comment on “High Temperature Shock Tube Study of the Reactions $\text{CH}_3 + \text{OH} \rightarrow \text{Products}$ and $\text{CH}_3\text{OH} + \text{Ar} \rightarrow \text{Products}$ ”

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In [1], experiments are performed on the title reactions to determine the rate coefficients for these reactions as a function of temperature. The authors' result for the reaction $\text{CH}_3 + \text{OH} \rightarrow \text{products}$ is very important to understanding the acetylene–methane chemistry in the postflame region of moderately rich ($\Phi = 1.5$), atmospheric pressure, nonsooting, hydrocarbon–air flames [2]. Measured hydrocarbon species profiles in rich, laminar, flat flames fueled by methane, ethane, ethylene, or propane in [2] show that both acetylene and methane persist in the postflame gas to a distance greater than 1.0 cm beyond the flame front, which is located ~ 0.15 cm above the burner. Acetylene is converted into methane in this region, resulting in rising methane concentrations as the distance from the flame front increases for all fuels except methane. The amount by which the product methane rises depends upon the fuel used. In the case of ethylene fuel over the distance range 0.6–1.3 cm above the burner, the acetylene mole fraction decreases from 2100 to 1300 ppm, while the methane mole fraction increases from 900 to 1200 ppm. Other hydrocarbon species measured in the

postflame gas include ethylene, allene, propyne, and diacetylene all at mole fractions less than 20 ppm. These species are in near partial equilibrium with acetylene.

The chemistry of acetylene consumption and methane formation in the postflame region was modeled in [2] using an extensive mechanism (with the best estimates of the rate constants available at the time) including these specific reactions: (1) $\text{OH} + \text{C}_2\text{H}_2 \rightarrow \text{ketene} + \text{H}$; (2) $\text{H} + \text{ketene} \rightarrow \text{CH}_3 + \text{CO}$; (3) $\text{CH}_3 + \text{OH} \rightarrow \text{CH}_2\text{OH} + \text{H}$; and (4) $\text{CH}_3 + \text{H}_2\text{O}$ (or H_2) $\rightarrow \text{CH}_4 + \text{OH}$ (or H). These reactions provide a path that can produce methane via OH reaction with acetylene. Reaction (3) was chosen in this model to be the primary sink for methyl radicals and, as such, is critical to the determination of the methane profile in these flames. Also included in the mechanism was the reversible reaction $\text{CH}_3 + \text{OH} \rightleftharpoons \text{CH}_2 + \text{H}_2\text{O}$. In the postflame gas (which has a high H_2O concentration), this reaction was not a significant sink for CH_3 in the model but rather participated in establishing the partially equilibrated hydrocarbon radical pool. The rate constant for reaction (3) was estimated to be $k_3 = 1.4 \times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ based on the shape of the methane profile in the propane–air flame in [2] at 1700 K with an estimated error of $\sim 30\%$. Perhaps fortuitously, this rate constant does agree well with the rate constant of

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$k_3 = 1.5 \times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ measured in [1] at 1426 K, although it is my understanding that products were not identified. It also agrees with the theoretical fit to the data in Fig. 4 of [1], which was published by Jasper et al. [3] earlier. This theoretical paper by Jasper et al. estimates that at 1700 K reaction (3) comprises $\sim 35\%$ of the total reaction products of the overall reaction $\text{CH}_3 + \text{OH} \rightarrow$ products.

The rate constant for the CH_3 sink represented by reaction (3) in [2] is critical to the modeling of the chemistry of rich combustion in the postflame region. This chemistry influences emissions from practical combustion systems such as the automotive engine [4]. Methane and acetylene emissions increase rapidly as the fuel mixture is enriched beyond the stoichiometric fuel–air ratio in spark-ignited engines because of the persistence of acetylene and methane in the postflame gases of rich flames [5,6]. The authors of [1] are to

be commended for their important study of the rate constant of the $\text{CH}_3 + \text{OH}$ reaction. An experimental determination of the products of this reaction would also be very important.

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