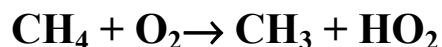


# Initiation in CH<sub>4</sub>/O<sub>2</sub>: High temperature Rate Constants for



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## Initiation in CH<sub>4</sub>/O<sub>2</sub>: High temperature Rate Constants for CH<sub>4</sub> + O<sub>2</sub> → CH<sub>3</sub> + HO<sub>2</sub>

About five years ago, we measured rate constants at high temperature for the initiation reaction in H<sub>2</sub>/O<sub>2</sub>,



using O-atom atomic resonance absorption spectrometry (ARAS) as the method of detection.<sup>1</sup> In this study, rate constants for the primary initiation process in CH<sub>4</sub> oxidation



has been measured in a reflected shock tube apparatus between temperatures of 1667-2018 K using multi-pass absorption spectrometric detection of OH-radicals at 308 nm. [OH]<sub>t</sub> was observed as a product of reaction (2) after rapid dissociation of HO<sub>2</sub>, yielding H-atoms which are instantaneously converted to OH via H + O<sub>2</sub> → OH + O.

The present work utilizes 32 optical passes corresponding to a total path length of 2.8 m. This configuration gives a signal to noise ratio of unity at 5 × 10<sup>11</sup> radicals cm<sup>-3</sup>. Hence, kinetics experiments could be performed at conditions of low [CH<sub>4</sub>]<sub>0</sub> (~ 75-100PPM) thereby reducing secondary chemistry substantially. Possible implications due to CH<sub>4</sub> dissociation contributing to the OH formation rates at high-T were considered. This reaction has been accurately measured under similar conditions in our laboratory<sup>2</sup> and minor perturbations to that rate do not affect our conclusions on reaction (2).

Over the temperature range, 1667-2018 K, the rate constants for the title reaction can be represented by the Arrhenius expression,

$$k_2 = 2.86 \times 10^{-10} \exp(-27194 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \quad (3)$$

The present experimental results for k<sub>2</sub>, compared with a recent variational Transition State Theory calculation using the VARIFLEX code for the reverse reaction transformed through equilibrium constant, clearly overlap each other within experimental error. The new values for k<sub>2</sub> obtained in this study are 8-10 times higher than the values used in the popular kinetics codes GRI-Mech 3.0 and Leeds Methane mechanism version 1.5.

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