Initiation in CH_4/O_2: High temperature Rate Constants for $CH_4 + O_2 \rightarrow CH_3 + HO_2$

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About five years ago, we measured rate constants at high temperature for the initiation reaction in H_2/O_2,

$$H_2 + O_2 \rightarrow HO_2 + H, \qquad (1)$$

using O-atom atomic resonance absorption spectrometry (ARAS) as the method of detection.[1] In this study, rate constants for the primary initiation process in CH_4 oxidation

$$CH_4 + O_2 \rightarrow CH_3 + HO_2, \qquad (2)$$

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. $[OH]_t$ was observed as a product of reaction (2) after rapid dissociation of HO_2, yielding H-atoms which are instantaneously converted to OH via $H + O_2 \rightarrow OH + O$.

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^{11} radicals cm^{-3}. Hence, kinetics experiments could be performed at conditions of low $[CH_4]_0$ (~ 75-100PPM) thereby reducing secondary chemistry substantially. Possible implications due to CH_4 dissociation contributing to the OH formation rates at high-T were considered. This reaction has been accurately measured under similar conditions in our laboratory[2] 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,

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

The present experimental results for k_2, 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_2 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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