

Analysis of the kinetics of OH from the CH₃OCH₃ + OH reaction in the presence of O₂ in the temperature range 550-700 K and 1-3 atm

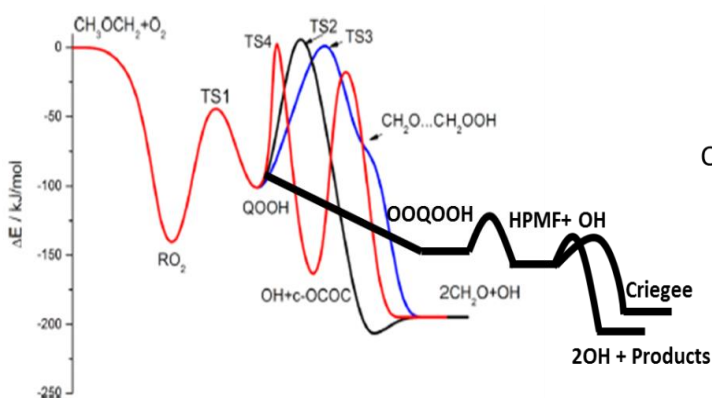
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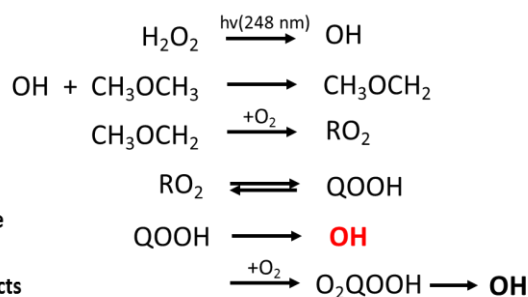
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Dimethyl ether (CH₃OCH₃, DME) has considerable potential as a fuel, but there are significant uncertainties in the mechanism of its important low temperature combustion. A key intermediate species is OH radical. In this study the important initial reactions in the oxidation of DME have been investigated by monitoring the kinetics of the OH radical in the presence of DME and O₂ over the ranges of temperature, 550-700 K, and total pressure, 1-3 atm. These measurements have been performed in our newly constructed high-temperature, high-pressure FAGE (fluorescence assay by gas expansion) apparatus, where O₂ can be the major constituent of the system.¹



Potential Energy Surface of the CH₃OCH₂+O₂ system



Reaction scheme

OH propagation from CH₃OCH₂ + O₂ reaction when [O₂] is small was extensively studied in our previous investigation,² (red PES). The current work is mainly focused on the OH kinetics in the presence of high [O₂] (black PES):



which potentially leads to chain branching. At $T < 650$ K the OH traces were single exponential. Only when temperature was further increased that OH traces exhibiting biexponential behavior were observed giving strong evidence for OH propagation via QOOH + O₂. These data are currently being analyzed in conjunction with ab initio/master equation calculations of the CH₃OCH₂ + O₂ system to provide a set of pressure and temperature dependent phenomenological reaction rate constants. Already, it is clear from these data there are very significant discrepancies between our experimental measurements and model predictions based on the current literature. Our current results indicate the literature overestimates propagation or branching. Potential reasons may derive from the calculated rate constant for R1 being much smaller and that HMPF has several decomposition channels.

References

- (1) Stone, D. Blitz, M.A., Ingham, T., Onel, L. Medeiros, D.J. and Seakins P.W. *Rev Sci Inst.*, **2016**, in press.
- (2) Eskola, A.J., Carr, S.A., Shannon, R.J., et al., *J. Phys. Chem. A*, **2014**, 118, 6773–6788.