Chemical Kinetics of the Reactions $H + O_2 \leftrightarrow HO_2$, $H + OH \leftrightarrow H_2O$, and $OH + OH \leftrightarrow H_2O_2$ Involved in Combustion of H_2 at Gas-Turbine Conditions

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Summary

The reactions $H + O_2 \leftrightarrow HO_2$, $H + OH \leftrightarrow H_2O$, and $OH + OH \leftrightarrow H_2O_2$ have been characterized using quantum chemistry (the CASPT2 model employing the aug-cc-pVDZ and aug-cc-pVTZ basis sets). High-pressure limiting rate coefficients for the reactions have been calculated using variable reaction coordinate transition state theory. The pressure dependence of the reactions were investigated using a two-dimensional master equation.

Calculated reaction rate coefficients:

- $k_\infty(H+O_2) = (25T^{-0.367} + 0.075T^{0.702}) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}
- $k_\infty(H+OH) = 4.17\times10^{-11}\, T^{0.234}\exp(57.5/T)$ cm^3 molecule^{-1} s^{-1}
- $k_\infty(OH+OH) = 2.17\times10^{-10}\, T^{-0.30}\exp(152/T)$ cm^3 molecule^{-1} s^{-1}
- $k_0(H+O_2+Ar) = 7.1\times10^{-29}T^{-1.37}\exp(-119/T)$ cm^6 molecule^{-2} s^{-1}
- $k_0(H+O_2+N_2) = 1.6\times10^{-27}T^{-1.7}\exp(-258/T)$ cm^6 molecule^{-2} s^{-1}
- $k_0(H+OH+Ar) = 2.2\times10^{-26}T^{-1.92}\exp(-405/T)$ cm^6 molecule^{-2} s^{-1}
- $k_0(H+OH+N_2) = 6.8\times10^{-26}T^{-1.99}\exp(-392/T)$ cm^6 molecule^{-2} s^{-1}

$H + O_2 + M \leftrightarrow HO_2 + M$

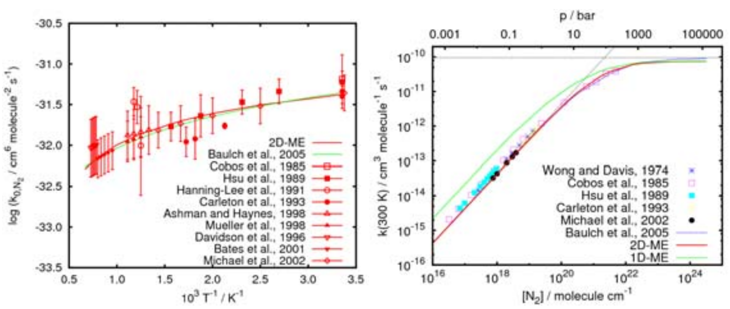

Figure 1. Low-pressure limiting rate coefficient as a function of temperature (*left*) and falloff curve (*right*) for the reaction $H + O_2 + N_2 \rightarrow HO_2 + N_2$.

$OH + OH \leftrightarrow H_2O_2$

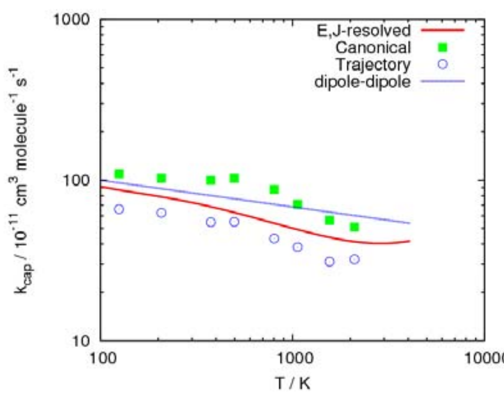

Figure 2. Capture rate coefficient as a function of temperature for the reaction $OH + OH \rightarrow H_2O_2$.

Motivation

It is evident that use of fossil fuels has contributed to an unequivocal warming of the climate system. Use of H_2 to create "decarbonized fuels" may significantly reduce CO_2 emissions from the power production industry. Utilization of H_2 as gas turbine fuel necessitates accurate description of the combustion process at elevated pressures. However, even apparently small differences between the available chemical mechanisms for H_2 combustion can have significant effect on predicted flame properties. To help improve the chemical insight into the combustion of H_2, we have initiated a quantum chemistry study of the reactions $H + O_2 \leftrightarrow HO_2$, $H + OH \leftrightarrow H_2O$, and $OH + OH \leftrightarrow H_2O_2$ at conditions relevant for gas turbines.

$H + OH + M \leftrightarrow H_2O + M$

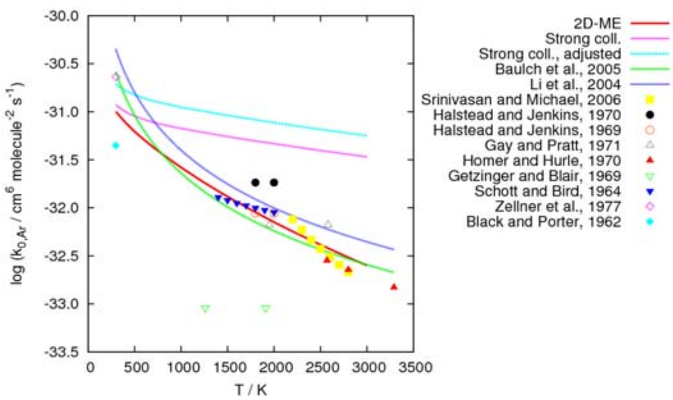

Figure 3. Low-pressure limiting rate coefficient as a function of temperature for the reaction $H + OH + Ar \rightarrow H_2O + Ar$.

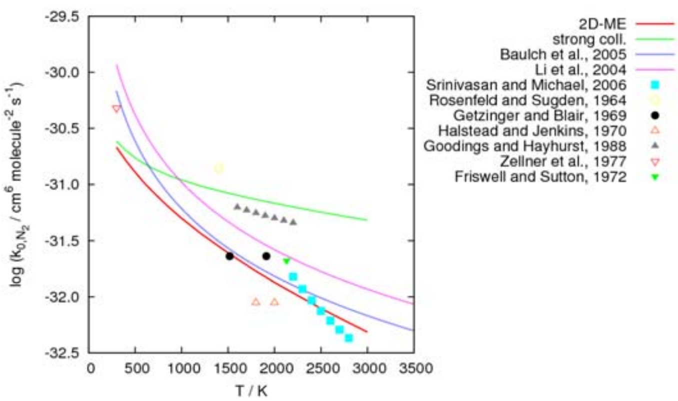

Figure 4. Low-pressure limiting rate coefficient as a function of temperature for the reaction $H + OH + N_2 \rightarrow H_2O + N_2$.

Acknowledgement

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