Hydrogen – Oxygen Kinetic Model Update

"Comprehensive H_2/O_2 Kinetic Model for High-Pressure Combustion"

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An updated H_2/O_2 kinetic model based on that of Li *et al*. [*Int. J. Chem Kin*. 36 (2004), 566-575] is presented and tested against a wide range of combustion targets. The primary motivations of the model revision are to incorporate recent improvements in rate constant treatment as well as resolve discrepancies between experimental data and predictions using recently published kinetic models in dilute, high-pressure flames.

Attempts are made to identify major remaining sources of uncertainties, in both the reaction rate parameters and the assumptions of the kinetic model, affecting predictions of relevant combustion behavior. With regard to model parameters, present uncertainties in the temperature and pressure dependence of rate constants for HO_2 formation and consumption reactions are demonstrated to substantially affect predictive capabilities at high-pressure, low-temperature conditions. With regard to model assumptions, calculations are performed to investigate several reactions/processes that have not received much attention previously. Results from ab initio calculations and modeling studies imply that inclusion of $H + HO_2 = H_2O + O$ in the kinetic model might be warranted, though further studies are necessary to ascertain its role in combustion modeling. Additionally, it appears that characterization of nonlinear bath-gas mixture rule behavior for $H + O_2 (+M) = HO_2(+M)$ in multi-component bath gases might be necessary to predict high-pressure flame speeds within ~15%.

The updated model is tested against all of the previous validation targets considered by Li *et al*. as well as new targets from a number of recent studies. Special attention is devoted to establishing a context for evaluating model performance against experimental data by careful consideration of uncertainties in measurements, initial conditions, and physical model assumptions. For example, ignition delay times in shock tubes are shown to be sensitive to potential impurity effects, which have been suggested to accelerate early radical pool growth in shock tube speciation studies. Additionally, speciation predictions in burner-stabilized flames are found to be more sensitive to uncertainties in experimental boundary conditions than to uncertainties in kinetics and transport. Predictions using the present model adequately reproduce previous validation targets and show substantially improved agreement against recent high-pressure flame speed and shock tube speciation measurements.

Notes:

The present kinetic model is a substantial update of the earlier Li *et al*. Model. The supplemental data compares the predictions of this model against a wide range of targets, along with predictions of numerous other hydrogen oxidation models present in the literature at the time of publication. The manuscript for this paper was accepted for publication in the International Journal of Chemical Kinetics on June 24, 2011. The published version of this manuscript will be substituted for the current manuscript as soon as it is available. At present, please quote reference to this work as "M.P. Burke, M. Chaos, Y. Ju, F.L. Dryer, and S.J. Klippenstein, "Comprehensive H2/O2 Kinetic Model for High-Pressure Combustion," *International Journal of Chemical Kinetics* (2011) accepted for publication.