Title: Development of Comprehensive Detailed and Reduced Reaction Mechanisms for Synagas and Hydrogen Combustion

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ABSTRACT

Objective

This project aims to develop tools necessary for the design of future coal derived syngas and hydrogen (SGH) fueled combustion turbines. A set of benchmark experiments and computations will be carried out to map: the flame speeds, autoignition characteristics, and extinction limits of SGH-oxidizer mixtures over a wide range of mixture compositions, inlet temperatures, and pressures. These global values will in turn be used to develop comprehensive detailed and reduced kinetic models for $H_2/CO/H_2O/O_2/N_2$ chemistry. Additionally, the resulting experimental database will be of practical use in determining the desired syngas compositions for optimal IGCC operation, as well as improving the design and operation of internal combustion engines fueled by hydrogen.

Accomplishments to Date

The kinetic mechanism for the combustion of $CO+H_2$ mixtures at high pressures in the range 15–50 bar and compressed temperatures from 950 to 1100 K was evaluated by experimental and numerical investigations with emphasis on global uncertainty analysis which simultaneously took into account the uncertainty associated with all the rate constants. Deficiencies of existing kinetic mechanisms in predicting the measured ignition delays from a rapid compression machine was noted, and through global uncertainty analysis it was shown that the reaction rate constant recommended by Baulch *et al*. for the HO_2+CO reaction, at temperature around 1000 K, could be up to a factor of 10 too high and that lowering this rate could correct the qualitative anomaly between experiment and numerical prediction.

The reaction $CO+HO_2\bullet \rightarrow CO_2 + \bullet OH$ was subsequently studied using the single-reference CCSD(T) method with Dunning's cc-PVTZ and cc-PVQZ basis sets and multireference CASPT2 methods. It was found that the classical energy barriers are about 18 and 19 kcal/mol for $CO+HO_2\bullet$ addition following the *trans* and *cis* paths. The HOOC•H adduct has a well defined local energy minimum in the *trans* configuration, but the *cis*-conformer is either a very shallow minimum or an inflection point on the potential energy surface. This observation led us to treat the *cis*-pathway by the classical transition state theory and the *trans*-pathway by a Master Equation analysis. The computation showed that the overall rate is independent of pressure up to 500 atm. Upon a careful treatment of the hindered internal rotations in the HOOC•H adduct and relevant transition states, the rate coefficient expression for this reaction was obtained as k (cm^3/mol.s) = $1.6 \times 10^5 T^{2.18} e^{-9030/T}$ for $300 \leq T \leq 2500$ K.

Preliminary experiments were also conducted to determine the effect of water addition on ignition characteristics of H_2/CO mixtures in a rapid compression machine while keeping the total H_2+CO mole fraction as constant. It was noted that the small amount of water addition does not alter the ignition delay of investigated mixtures. In contrast, the kinetic models showed a relatively stronger retardation of ignition due to the addition of water.

The high pressure oxidation of dilute CO mixtures doped with 150–200 ppm of H_2 behind reflected shock waves up to 600 atm was also examined. The experimental data was collected in the UIC high pressure single pulse shock tube. Simulations using a previously published reaction model showed that within experimental error the kinetic model is able to capture the experimental trends for the lower pressure data sets (average nominal pressures of 24 and 43 bars). However, the model under-predicts the CO and O_2 decay and subsequent CO_2 formation for the higher pressure data sets (average nominal pressures of 256 and 450 bars). With updated rate parameters for $HO_2+OH=H_2O+O_2$ the model was found to reconcile the elevated pressure data sets.

In addition, the counterflow burner apparatus has been adequately adapted and characterized for investigations of combustion characteristics, such as laminar flame speeds and extinction stretch rates, of SGH mixtures.

Future Work

Detailed experimental data for combustion characteristics of SGH mixtures will be acquired in a rapid compression machine and counterflow burner. Rapid compression machine experiments will cover a wide range of physical conditions, with special emphasis on the effects of CO_2 and H_2O addition on the autoignition of H_2/CO mixtures. In addition, the counterflow twin-flame apparatus will be employed for the measurements of laminar flame speed and strain-induced extinction limits of premixed SGH flames.

The kinetic mechanism will be subsequently assessed against the newly acquired experimental data, thereby enabling re-evaluation and optimization of rate constants and mechanism. In particular, ab initio quantum chemistry calculation and master equation modeling will be conducted for certain key reactions. These reactions include, for example, $HO_2+HO_2\rightarrow H_2O_2+O_2$ and $HO_2+OH\rightarrow H_2O+O_2$, all of which have a notable influence on SGH oxidation rates under high-pressure, low-to-intermediate temperature conditions. All of the reactions in question have complex temperature and pressure dependences that cannot be easily resolved through mechanism optimization.

List of Publications/Presentations

1. G. Mittal, C.J. Sung, M. Fairweather, A.S. Tomlin, J.F. Griffiths, and K.J. Hughes, "Significance of the HO_2+CO Reaction during the Combustion of CO+H_2 Mixtures at High Pressures," *Proceedings of the Combustion Institute*, 2007, Vol. 31, 419-427.
2. R. Sivaramakrishnan, A. Comandini, R.S. Tranter, K. Brezinsky, S.G. Davis, and H. Wang, "Combustion of CO/H_2 mixture at elevated pressures," *Proceedings of the Combustion Institute*, 2007, Vol. 31, 429-437.
3. X. You, E. Goos, C.J. Sung, and H. Wang, "Reaction kinetics of $CO+HO_2\rightarrow CO_2+OH$ ab initio study and master equation modeling," work-in-progress poster, 31st International Symposium on Combustion, Heidelberg, Germany, August 2006.
4. G. Mittal and C.J. Sung "Ignition of moist syngas in a rapid compression machine", 5th US Combustion Meeting, San Diego, March 2007.
5. X. You, H. Wang, E. Goos, C.J. Sung, and S. J. Klippenstein "Reaction kinetics of $CO+HO_2\rightarrow$ products: ab initio study and master equation modeling," 5th US Combustion Meeting, San Diego, March 2007.
6. X. You, H. Wang, E. Goos, C.J. Sung, and S. J. Klippenstein "Reaction kinetics of $CO+HO_2\rightarrow$ products: ab initio study and master equation modeling," *Journal of Physical Chemistry A*, in press.
7. C.J. Sung and C.K. Law "Fundamental combustion properties of H_2/CO mixtures: Ignition and flame propagation at elevated pressures," *Combustion Science and Technology*, submitted.

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1. Apurba K.Das, graduate student in the Department of Mechanical and Aerospace Engineering, Case Western Reserve University.
2. Xiaoqing You, graduate student in the Department of Aerospace and Mechanical Engineering, University of Southern California.