

# COMPREHENSIVE KINETIC MECHANISMS FOR C<sub>1</sub> SPECIES COMBUSTION

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In the hierarchical development of kinetic mechanisms for large hydrocarbons, the reaction systems involving C<sub>1</sub> species represent the next level of complexity beyond the thoroughly studied reactions of H<sub>2</sub>/O<sub>2</sub> mixtures. Encompassing our recently updated H<sub>2</sub>/O<sub>2</sub> mechanism (Li et al., *Int. J. Chem. Kinet.*, submitted), we have revisited the CO/H<sub>2</sub>/O<sub>2</sub>, CH<sub>2</sub>O/O<sub>2</sub>, and CH<sub>3</sub>OH/O<sub>2</sub> systems, considering recent kinetic and thermochemical results. The mechanisms were tested using new experimental targets as well as those employed in our earlier publications (e.g. Held and Dryer, *Int. J. Chem. Kinet.*, 1998, 30, 805).

The most important revisions to our prior published mechanisms involve the rate constant descriptions for CO + OH = CO<sub>2</sub> + H, (R1), and HCO + M = H + CO + M, (R2). The recently published RRKM calculations for (R1) (e.g. Senesiain et al., *Int. J. Chem. Kinet.*, 2003, 35, 464) universally predict values higher than experimental measurements at low to intermediate temperatures. A weighted least squares fitting of literature experimental data for (R1) yields  $k_{1f} = 2.23 \times 10^5 T^{1.89} \exp(-583/T)$ . The decomposition reaction (R2) and the abstraction reaction, HCO + O<sub>2</sub> = HO<sub>2</sub> + CO, (R3), are the main pathways to generating CO during the high temperature combustion of hydrocarbons. The uncertainties of the new rate measurements for these two reactions (Friedrichs et al. *Phys. Chem. Chem. Phys.*, 2002, 4, 5778; DeSain et al. *Chem. Phys. Lett.*, 2001, 347, 79) are sufficiently small to exclude the earlier work of Timonen et al. (*J. Phys. Chem.*, 1987, 91, 5325 and 1988, 92, 651). Premixed flame speeds of small-hydrocarbon oxygenate/air mixtures (methanol, dimethyl ether, ethanol) are particularly sensitive to (R2) and (R3), however, the new expressions result in significantly degraded flame speed predictions for these systems. The sensitivity analysis of Zhao et al. (*Int. J. Chem. Kinet.*, submitted) demonstrates that flame speeds are most sensitive to the values of (R2) and (R3) in the temperature ranges 1350-2000 K and 1200-1900 K, respectively, well above the range of conditions of the recent measurements. We adopted a weighted least squares fitting of literature data ( $k_{2f} = 4.75 \times 10^{11} T^{0.66} \exp(-7485/T)$ ) spanning the appropriate temperatures for (R2). Since there are few experimental measurements at high temperatures for  $k_{3f}$  (NIST kinetics database, 2004), the recommendation of Timonen et al. was adopted as in our earlier models. For the CH<sub>2</sub>O/O<sub>2</sub> and CH<sub>3</sub>OH/O<sub>2</sub> systems, literature review of other reactions led us to adopt the recommendations of some recent kinetics publications.

The present C<sub>1</sub>/O<sub>2</sub> mechanism has been compared against a wide range of experimental conditions (300-3000 K, 0.15-9.6 atm,  $\phi = 0.4-6.1$  for CO oxidation; 300-2150 K, 0.03-12.0 atm,  $\phi = 0.005$  to pyrolysis for CH<sub>2</sub>O; 300-2200 K, 1.0-20 atm,  $\phi = 0.05-6.0$  for CH<sub>3</sub>OH oxidation) and for laminar-premixed flame speeds, shock tube ignition delay, and flow reactor species time history experiments. Very good agreement of the model predictions with the experimental measurements was achieved in all comparisons.